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Synthesis of Tungsten Carbonyl and Nitrosyl Complexes of Monodentate and Chelating Aryl-*N*-sulfonylphosphoramides, the First Members of a New Class of Electron-Withdrawing Phosphine Ligands. Comparative IR and ^{13}C and ^{31}P NMR Study of Related Phosphorus Complexes

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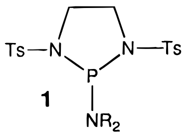
Reaction of *N*,*N*′-bis(tolylsulfonyl)-1,2-diaminoethane with $PhPCl_2$ gives in 62% yield the phosphonous diamide 2-phenyl-1,3-bis(*p*-tolylsulfonyl)-1,3,2-diazaphospholidine (**4**, “TosL”) and with Ph_2PCl in 43% yield the diphosphinous amide *N*,*N*′-bis(diphenylphosphino)-*N*,*N*′-bis(*p*-tolylsulfonyl)-1,2-ethanediamine (**5**, “diTosL”). Reaction of **4** with (THF)$W(CO)_5$ gives (TosL)$W(CO)_5$ (**6**) in 77% yield, and reaction of **5** with *trans*-$BrW(CO)_4NO$ gives *cis, cis, trans*-(diTosL)$W(CO)_2(NO)Br$ (**8**) in 86% yield. The IR, ^{13}C NMR, and ^{31}P NMR spectra of **4**, **5**, **6**, and **8** are compared to those of a variety of compounds including $LW(CO)_5$ (L = PMe_3, PPh_3, $PPh(NEt_2)_2$, $P(OMe)_3$, $P(CF_3)_3$), $L_2W(CO)_2(NO)Br$ ($L_2 = Ar_2PCH_2CH_2PAr_2$ (Ar = Ph (diphos), C_6F_5 (diphos-F_{20})), $(CH_3CN)_2$), and the free ligands as appropriate. The IR data are interpreted to suggest a relative ordering of ligand acceptor ability of $P(CF_3)_3 > \mathbf{4} \approx P(OMe)_3 > PPh_3 \approx PPh(NEt_2)_2$ and a relative ordering of ligand donor ability of $PPh(NEt_2)_2 \geq P(OMe)_3 > PPh_3 > \mathbf{4} > P(CF_3)_3$. The chelating ligand diTosL is about as electron-withdrawing as diphos-F_{20}, on the basis of the IR data. The ^{31}P NMR data qualitatively support the conclusion that TosL and diTosL are highly electron-withdrawing ligands, on the basis of $^1J_{PW}$. The ^{13}C data do not permit any such generalizations, although the spectra of the diphosphine ligands and adducts are of interest due to the observation of “virtual coupling” that surprisingly can be simulated only as ABX rather than AA′X spin-systems.

Introduction

Syntheses of transition metal ligands that mimic the strong π-acidity of carbon monoxide, but are larger and so can play a steric role in reactivity at the metal, have focused on fluorinated phosphines,[1−4] although a recent report describes the use of *N*-pyrrolylphosphines.[5] Another strongly electron-withdrawing group that might affect phosphorus σ-donation and π-acidity is the sulfonyl group. Rather than attempt to directly attach the sulfonyl group to phosphorus, however, we envisioned the presence of an intermediate nitrogen atom to give *N*-sulfonylphosphoramides as our target ligands. While phosphoramides of the type $R_nP(NR'_2)_{3-n}$ ($n = 0,1,2$) are well-known[6−8] as is the use of *primary* sulfonamides to generate $R_3P{=}NSO_2R$ species,[6] we required *secondary* sulfonamides to generate the desired ligands. Reaction with phosphorus chlorides in a manner analogous to secondary amines[9−11] seemed straightforward, but since sulfonamides are relatively acidic compounds, the possibility existed that the nitrogen would not be nucleophilic enough to displace chloride from phosphorus. A small number of fully heteroatom-substituted phosphorus compounds such as **1**[12,13] and **2**[14−16] have been prepared in this manner and reported recently, but we are aware of only a single aryl-substituted analog (**3**), which was prepared using *p*-tolylsulfonyl isocyanate.[17] None of these compounds have been considered for study as ligands in transition metal compounds. In fact, we report here that the synthesis of aryl-substituted *N*-sulfonylphosphor-



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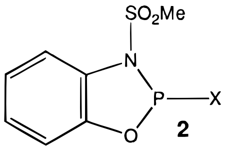

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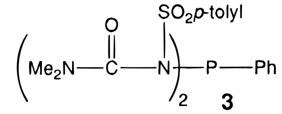
X = NR_2, OR



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amides is simple, and describe the first examples of such a phosphine, including a bis(sulfonamido)phenylphosphine ligand and a bis((diphenylphosphino)sulfonamido)ethane ligand, the synthesis of tungsten complexes of these ligands, and spectroscopic data in support of the thesis that they are indeed strongly electron-withdrawing.

Experimental Section

General Data. All manipulations of air-sensitive compounds were carried out either in a Vacuum Atmospheres inert atmosphere drybox under recirculating nitrogen or by using standard Schlenk techniques. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on an IBM/Bruker WP-200SY spectrometer and a Bruker DPX-400 spectrometer; chemical shifts are reported relative to TMS or residual hydrogens in CD_2Cl_2 (δ 5.32) or $CDCl_3$ (δ 7.24), to $CDCl_3$ at 77.0 ppm for ^{13}C NMR, and to external 85% H_3PO_4 at 0 ppm (positive values downfield) for ^{31}P NMR. ^{13}C NMR data are collected in Table 1 and ^{31}P NMR data in Table 2. Infrared spectra were obtained on a Mattson Galaxy 4020 FT-IR spectrometer with 0.1 mm NaCl solution cells. Elemental analyses were performed by Desert Analytics, Tucson, AZ, and Quantitative Technologies, Inc., Whitehouse, NJ. Mass spectra (EI, 70 eV) were obtained on an HP5988A spectrometer.

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; $CDCl_3$ and CD_2Cl_2 were vacuum-transferred from phosphorus pentoxide.

Silica gel (200−400 mesh) was dried for several hours under vacuum while heating with a heat gun and was transferred under vacuum into the drybox. $PhPCl_2$, Ph_2PCl (Aldrich), 1,2-bis(dipentafluorophenylphosphino)ethane (Strem), and $W(CO)_6$ (Pressure Chemical) were used as received, and *trans*-$BrW(CO)_4NO$ (contaminated by ∼26% by weight of $W(CO)_6$ on the basis of elemental analysis) was prepared as previously described.[19,20]

2-Phenyl-1,3-bis(*p*-tolylsulfonyl)-1,3,2-diazaphospholidine (4, TosL). Under a nitrogen atmosphere, a solution of 1.17 mL of $PhPCl_2$ (8.62 mmol) in 40 mL of anhydrous ether was added dropwise over a 50 min period to an ice-cooled suspension of 3.18 g of $CH_3C_6H_4SO_2N(H)CH_2CH_2N(H)SO_2C_6H_4CH_3$[21] (8.63 mmol) and 3.0 mL of Et_3N (distilled under N_2 from CaH_2; 21.5 mmol) in 220 mL of anhydrous ether. The mixture was then stirred at room temperature for an additional 30 min, and then the solvent was removed on a rotary evaporator. The resultant white powder was purified by dissolving the residue in 50 mL of CH_2Cl_2 and passing the solution through a ∼100 mL pad of silica gel packed in CH_2Cl_2 on a 150 mL sintered glass frit. The product was eluted with 300 mL more CH_2Cl_2, and the solvent removed on a rotary evaporator to give 2.54 g (62% yield) of **4** as a spectroscopically pure white powder. Material submitted for elemental analysis was crystallized from 3:1 CH_2Cl_2/hexane at −40 °C in the glovebox. ^{1}H NMR ($CDCl_3$): δ 7.69 (m, 2H, Ph), 7.63 (d, $J = 8.2$ Hz, 4H, Ts), 7.45 (m, 3H, Ph), 7.18 (d, $J = 8.2$ Hz, 4H, Ts), 3.50 (m, 2H, $C(H_a)H_bC(H_a)H_b$), 3.20 (m, 2H, $C(H_a)H_bC(H_a)H_b$), 2.44 (s, 6H, CH_3). MS: 410 (13%, $M^+ - SO_2$), 409 (17%, $M^+ - HSO_2$), 397 (2%, $P(N(Ts)CH_2CH_2NTs)^+$), 255 (72%, $M^+ - Ts - SO_2$), 155 (14%, Ts^+), 91 (100%, C_7H_7); the 20 eV MS of **4** was virtually the same as that at 70 eV. Anal. Calcd for $C_{22}H_{23}N_2O_4S_2P$: C, 55.69; H, 4.89; N, 5.90. Found: C, 55.44; H, 4.83; N, 5.94.

***N,N′*-Bis(diphenylphosphino)-*N,N′*-bis(*p*-tolylsulfonyl)-1,2-ethanediamine (5, diTosL).** Under a nitrogen atmosphere, 3.59 g (16.3 mmol) of Ph_2PCl was added dropwise to a solution of 3.00 g (8.14 mmol) of $CH_3C_6H_4SO_2N(H)CH_2CH_2N(H)SO_2C_6H_4CH_3$ and 2.06 g (20.35 mmol) of Et_3N in 50 mL of THF, and the mixture was heated at reflux for 21.5 h. After solvent removal on a rotary evaporator, the resultant pale yellow solid was taken up in 100 mL of benzene and filtered to remove $Et_3NH^+Cl^-$. Solvent removal on a rotary evaporator again gave a pale yellow powder (5.90 g) which was dissolved (in the air) in 20 mL of hot CH_2Cl_2 and then treated with 20 mL of hot anhydrous ether. Cooling to room temperature gave white crystals, and crystallization was completed at −10 °C overnight; filtration and rinsing with hexanes gave 2.57 g (43% yield) of **5** as air-stable white crystals. ^{1}H NMR ($CDCl_3$): δ 7.46 (d, $J = 8.2$ Hz, 4H, Ts), 7.36 (m, 4H, Ph), 7.29−7.20 (m, 16H, Ph), 7.18 (d, $J = 8.2$ Hz, 4H, Ts), 3.30 (br s, 4H, CH_2), 2.41 (s, 6H, CH_3). MS: 581 (1.5%, $M^+ - Ts$), 396 (2%, $M^+ - Ts - PPh_2$), 183 (100%, $TsNCH_2^+$). Anal. Calcd for $C_{40}H_{38}N_2O_4S_2P_2$: C, 65.20; H, 5.20; N, 3.80. Found: C, 64.84; H, 5.05; N, 3.75.

(TosL)W(CO)$_5$ (6). Tungsten hexacarbonyl (1.10 g, 3.13 mmol) and 80 mL of THF were placed in a 250 mL septum-capped flask with a magnetic stirring bar, which was placed in a water-cooled water bath and irradiated under a nitrogen atmosphere with a 450 W Hanovia medium pressure mercury lamp for 3 h. The resultant yellow solution was transferred via syringe into a solution of **4** (1.09 g, 2.30 mmol, 0.73 equiv based on $W(CO)_6$) in 10 mL of THF. No color change was observed, and the reaction mixture was stirred at room temperature under a nitrogen atmosphere and monitored periodically by IR. After 2.5 h little further change was observed, and the THF was removed on a vacuum line at room temperature. The resultant off-white powder was then warmed at ∼45 °C on the vacuum line to facilitate sublimation of unreacted $W(CO)_6$, and 1.65 g (90% yield based on **4**) of crude product was obtained. Attempts to crystallize this material from CH_2Cl_2, toluene, or mixtures of CH_2Cl_2/hexane and CH_2Cl_2/1,1,2-trichlorotrifluoroethane all failed. Final purification was achieved by filtration of a CH_2Cl_2 solution of the material through silica gel, eluting first with CH_2Cl_2 and then 1:1 CH_2Cl_2/THF, to give **5** (∼85% recovery after solvent removal and washing with hexane, 77% overall yield) as a spectroscopically pure white powder. A small sample of analytically pure material was obtained with difficulty by recrystallization from 3:1 hexane−CH_2Cl_2. IR (CH_2Cl_2): 2080 (m), 1952 cm^{-1} (s). ^{1}H NMR ($CDCl_3$): δ 7.56, 7.43, 7.32 (m, 5H, Ph), 7.12, 7.06 (AB quartet, $J =$ 8.5 Hz, 8H, Ts), 3.90 (m, (approximate quintet, $J = 5$ Hz), 2H, $C(H_a)H_bC(H_a)H_b$), 3.51 (m, (approximate quintet, $J = 5$ Hz), 2H, $C(H_a)H_bC(H_a)H_b$), 2.35 (s, 6H). MS: 410 (3%, $M^+ - SO_2$), 409 (5%, $M^+ - HSO_2$), 255 (30%, $M^+ - Ts - SO_2$), 155 (11%, Ts^+), 91 (100%, C_7H_7). Anal. Calcd for $C_{27}H_{23}N_2O_9S_2PW$: C, 40.62; H, 2.90; N, 3.51. Found: C, 40.76; H, 2.75; N, 3.44.

(bis(diethylamino)phenylphosphine)W(CO)$_5$ (7). A solution of 0.88 g (2.50 mmol) of $W(CO)_6$ in 80 mL of THF was photolyzed for 3 h as described above for **5**. A solution of $PPh(NEt_2)_2$ (0.57 g, 2.26 mmol, 0.9 equiv; prepared[10] in 52% yield as an air-stable spectroscopically pure cloudy white liquid, ^{1}H NMR ($CDCl_3$) δ 7.43, 7.3, 7.23 (m, 2H, 2H, 1H), 3.09 (dq, $^3J_{PH} = 9.6$ Hz, $^3J_{HH} = 7.0$ Hz, 8H), 1.11 (t, $J_{HH} = 7.0$ Hz, 12 H)) in 10 mL of THF was added by syringe to the $(THF)W(CO)_5$ solution, which was allowed to stir under a nitrogen atmosphere overnight. After solvent removal (vacuum line), the resultant yellow solid and clear oil was heated at 40 °C under vacuum for 2 h in order to partially remove unreacted $W(CO)_6$. The residue was then taken up in ∼10 mL of hexane, and the resulting solution filtered, concentrated, and filtered again to remove additional $W(CO)_6$. Attempted recrystallization at −40 °C gave ∼35 mg of a mixture of the product and more $W(CO)_6$. The remainder was applied to 15 mL of silica on a frit and eluted with 60 mL of hexane followed by 100 mL of 10% ether in hexane. The solvent was removed from this second fraction, and the resultant solid was taken up in the minimum amount of hexane, and the resulting solution was filtered and stripped to give 0.32 g (25% yield) of product as a pale yellow powder. IR (hexane): 2069.6 (m), 1977.4 (w), 1941.7 (s), 1935.9 (vs) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.52, 7.45, 7.36 (m, 5H), 3.36 (m, 4H), 3.23 (m, 4H), 1.16 (t, $J = 7.0$ Hz, 12H). MS: 576 (M^+). Anal. Calcd for $C_{19}H_{25}N_2O_5PW$: C, 39.60; H, 4.37; N, 4.86. Found: C, 39.77; H, 4.20; N, 4.77.

***cis, cis, trans*-(diTosL)W(CO)$_2$(NO)Br (8).** In the glovebox a solution of 226 mg of *trans*-$BrW(CO)_4NO$ (0.412 mmol) and 206 mg of **5** (0.280 mmol) in 4 mL of $CHCl_3$ was allowed to stand in a screw-capped 1 dram vial at room-temperature for 24 h. The solvent then was removed on a vacuum line to gave 320 mg of crude product as a yellow solid. Purification was carried out by column chromatography in the glovebox, and eluting with 9:1 CH_2Cl_2/hexane through silica gel to gave 261 mg (86% yield) of analytically pure **8** as a yellow

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Table 1. ^{13}C NMR Data[a]

compound	trans-CO ($^2J_{PC}$, $^1J_{CW}$[b])	cis-CO ($^2J_{PC}$, $^1J_{CW}$)	ΔJ_{ipso}[c]	PPh C_{ipso} ($^1J_{PC}$)	PPh C_2 ($^2J_{PC}$)	PPh C_3 ($^3J_{PC}$)	PPh C_4 ($^4J_{PC}$)	CH_2 ($^2J_{PC}$)	CH_3 ($^3J_{PC}$)	C_6H_4 (J_{PC})
PPh_3				137.11 (10.7)	133.71 (19.4)	128.47 (6.8)	128.69 (s)			
$PPh_3W(CO)_5$	199.12 (22.1)	197.25 (7.3, 125.5)	30.9	135.22 (41.6)	132.99 (12.3)	128.63 (9.7)	130.34 (s)			
$PPh(NEt_2)_2$				141.96 (3.4)	130.96 (16.0)	128.09 (3.1)	127.18 (1.4)	42.80 (16.5)	14.61 (2.8)	
$PPh(NEt_2)_2W(CO)_5$ (**7**)	200.32 (25.9)	197.31 (7.6, 126.4)	66.8	141.78 (70.2)	130.05 (11.2)	128.63 (8.8)	129.37 (s)	41.77 (5.3)	13.48 (4.1)	
TosL (**4**)				138.40 (32.1)	129.42 (20.5)	128.78 (5.6)	130.54 (s)	47.98 (5.7)	21.65 (s)	143.87 (br s, ipso), 135.80 (s, ipso), 129.74 (s, CH), 127.25 (2.6, CH)
(TosL)$W(CO)_5$ (**6**)	198.24 (37.2)	196.00 (8.0, 127.0)	−12.0	136.51 (20.1)	132.81 (17.9)	128.42 (10.7)	132.79 (s)	46.45 (s)	21.55 (s)	144.39, 135.37 (s, ipso), 129.45, 127.49 (s, CH)
$P(OMe)_3W(CO)_5$[d]	197.79 (37.6, 138.8)	195.18 (10.9, 125.7)							52.10 (3.4)[e]	
diphos				138.05 (13.4)[f,g]	132.72 (18.5)[h]	128.44 (6.4)[f]	128.64 (s)	23.81 (15, −11)[i]		
(diphos)$W(CO)_2$(NO)Br (**9**)	208.81 (48.5, 152.4)	208.81 (6.8)	29	132.39 (40.8)	132.79 (12.4)[f]	129.03 (10.5)[f]	130.82 (s)	26.82 (29.0, 10.7)[k]		
				131.73 (44.6, 1[j])	132.30 (10.5)[f]	128.46 (10.3)[f]	130.34 (s)			
diTosL (**5**)				134.66 (17.5)	132.56 (21.9)	128.49 (6.0)	127.48 (2.6)	49.20 (s)	21.55 (s)	143.43, 137.17 (s, ipso), 129.57, 129.40 (s, CH)
(diTosL)$W(CO)_2$(NO)Br (**8**)[i]	204.62 (55.2)	204.62 (0)	26	131.4 (44)[l]	133.82 (11.1)[f]	128.40 (9.7)[f]	131.18 (s)	51.66 (17, 6)[m]	21.56	144.32, 136.41 (s, ipso), 129.58, 127.16 (s, CH)
				130.76 (43.3)	132.74 (12.6)[f]	127.67 (10.3)[f]	131.08 (s)			

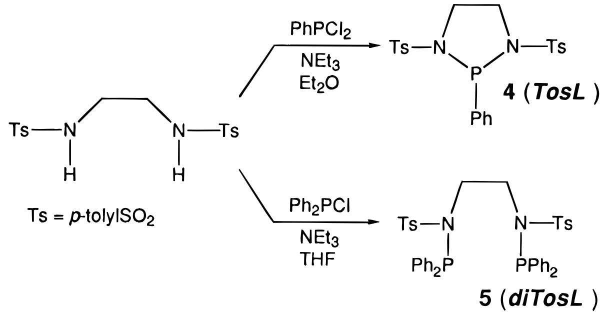
[a] Solvent: $CDCl_3$. All chemical shifts in ppm, all coupling constants in Hz, and all peaks are doublets except as noted. [b] In the cases where the trans-CO peak was too weak to permit observation of the tungsten satellites, $^1J_{PW}$ is not listed. [c] [$^1J_{PC}$(complexed ligand) − $^1J_{PC}$(free ligand)] for PPh ipso carbon. [d] ^{13}C NMR for free $P(OMe)_3$: 48.788 ppm, $^2J_{PC} = 10.9$ Hz. [e] $^2J_{PC}$. [f] "Triplet" in which the difference between the outer two lines, reported in the table, is $|J_{PC} + J_{P'C}|$. For C_{ipso}, C_2, and C_3, the long-range coupling (i.e. $J_{P'C}$) with two exceptions[g,j] is presumed to be zero and so the difference between the outer lines is J_{PC}. For diphos the central line is equal or greater than the outer lines in height: for **9** it is ~30% of the height, and for **8** it is roughly equal (see text). [g] The "triplet" is better fit by $^1J_{PC} \approx 16$ Hz, $^2J_{P'C} \approx -3$ Hz. [h] Quintet, in which the difference of lines 2 and 4 is $|J_{PC} + J_{P'C}|$ with weak "wings" at ±35.2 Hz from center peak; as in footnote *f*, $J_{P'C} = 0$ gives a good fit to the observed multiplet (see text).[i] $^1J_{PC}$, $^2J_{P'C}$, giving a "quartet", with two central lines split by 2.5 Hz and weak "wings" at ±37.3 Hz from center point. [j] $^4J_{PC}$, giving dd. [k] $^1J_{PC}$, $^2J_{P'C}$, giving a dd but with two additional weak peaks split by ~6 Hz about the center point (see text). [l] Assignment uncertain since (1) one peak of the doublet is partly obscured by the Ph C_4 singlets at 131.1−131.2, and (2) the four peaks could be assigned equally well as 131.28 ppm ($^1J_{PC} = 62.6$ Hz) and 130.8 ppm ($^1J_{PC} = 61$ Hz). The assignment in the table is preferred since the difference in chemical shift (~0.6 ppm) is comparable to those of the Ph C_2 and C_3 pairs of peaks. [m] "Triplet" with $|^1J_{PC} + ^2J_{PC}| = 23.1$ Hz.

Table 2. ^{31}P NMR Data

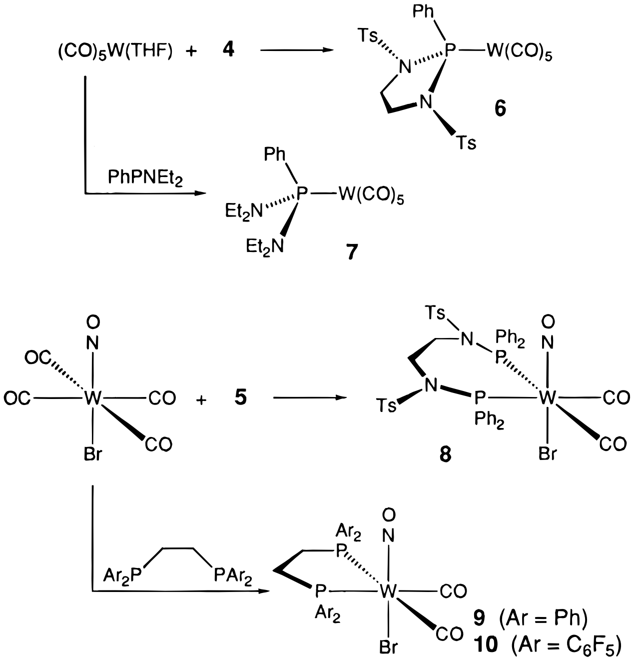
compound	chemical shift (ppm)^{a} free ligand	chemical shift (ppm)^{a} complex	$\Delta\delta_P$ (ppm)^{b}	$^{1}J_{PW}$ (Hz)	J_{PP} (Hz)^{c}
$PMe_3W(CO)_5$^{d,18}	−62.0	−39.8	22.2	230	
$PPh_3W(CO)_5$	−4.82	21.43	26.3	244.1	
$PPh(NEt_2)W(CO)_5$ (**7**)	97.67	105.41	7.7	289.5	
$P(CF_3)_3W(CO)_5$^{d,18}	−2.5	55.4	57.9	300	
(TosL)$W(CO)_5$ (**6**)	91.28	122.06	30.8	329.5	
$P(OMe)_3W(CO)_5$	141.61	141.02	−0.6	386.5	
(diphos)$W(CO)_2(NO)Br$ (**9**)	−12.03	32.74	44.8	249.1	3^{c}
(diphos-F_{20})$W(CO)_2(NO)Br$ (**10**)	−43.59	7.75	51.3	262.2	
(diTosL)$W(CO)_2(NO)Br$ (**8**)	60.37	77.11	16.7	270.8	5^{c}

^{a} $CDCl_3$ solution except as noted. ^{b} δ(complex) − δ(free ligand). ^{c} Derived from analysis of the ^{13}C NMR spectra; for free diphos, $^{3}J_{PP} \approx 35$ Hz and for free diTosL, $^{5}J_{PP} = 0$ Hz (see text). ^{d} C_6D_6 solution.

Scheme 1



Scheme 2



powder. IR (CH_2Cl_2): 2036 (s), 1968 (s), 1650 (br, m), 1598 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.91 (m, 4H, Ph), 7.69 (m, 4 H, Ph), 7.47 (m, 12H of Ph), 7.07 (d, $J = 8.2$ Hz, 4H, Ts), 6.82 (d, $J = 8.2$ Hz, 4H, Ts), 4.45 (m, 2H, $C(H_a)H_bC(H_a)H_b$), δ 4.03 (m, 2H, $C(H_a)H_bC(H_a)H_b$), δ2.38 (s, 6H, CH_3). Anal. Calcd for $C_{42}H_{38}N_3O_7P_2S_2WBr$: C, 46.43; H, 3.52; N, 3.87. Found: C, 46.50; H, 3.85; N, 3.94.

***cis, cis, trans*-(1,2-bis(dipentafluorophenylphosphino)ethane)-$(CO)_2W(NO)Br$ (10).** In the glovebox a solution of 227 mg of *trans*-$BrW(CO)_4NO$ (0.414 mmol) and 210 mg of 1,2-bis(dipentafluorophenylphosphino)ethane (diphos-F_{20}, 0.277 mmol) in 12 mL of $CHCl_3$ was stirred at room temperature for 23 h. The reaction mixture was filtered through a pad of Celite, and the solvent was removed on a vacuum line to gave 390 mg of crude product as a yellow solid. Purification was accomplished by flash chromatography on an 18 × 1 cm silica gel column eluting with CH_2Cl_2 to give 304 mg of yellow powder, followed by washing with hexane (in which **10** is slightly soluble) to give 186 mg (61% yield) of **10** as an analytically pure yellow powder. IR (CH_2Cl_2): 2054 (s), 1992 (s), 1650 (br, s), 1522 (s), 1483 (s) cm^{-1}. IR of diphos-F_{20} (CH_2Cl_2): 1642 (w), 1520 (s), 1482 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.33 (m, 2H, $C(H_a)H_bC(H_a)H_b$), 3.02 (m, 2H, $C(H_a)H_bC(H_a)H_b$). Anal. Calcd for $C_{28}H_4NO_3F_{20}P_2BrW$: C, 30.35; H, 0.36; N, 1.26. Found: C, 30.57; H, 0.52; N, 1.24

Results and Discussion

Synthesis of *N*-Sulfonylphosphoramides. Reaction of *N,N′*-bis(tolylsulfonyl)-1,2-diaminoethane with $PhPCl_2$ or Ph_2PCl in the presence of NEt_3 in ether or THF gave the desired phosphonous diamide “TosL” (**4**, 2-phenyl-1,3-bis(*p*-tolylsulfonyl)-1,3,2-diazaphospholidine) in 62% yield and the diphosphinous amide “diTosL” (**5**, *N,N′*-bis(diphenylphosphino)-*N,N′*-bis(*p*-tolylsulfonyl)-1,2-ethanediamine) in 43% yield, both as air-stable white crystalline solids (Scheme 1). Like the starting bis(sulfonamide), **4** and **5** are apparently polar materials as judged by their insolubility in ether, but other solubility properties are peculiar: **4** is benzene insoluble and slightly soluble in acetone, while **5** is insoluble in acetone and ethanol yet soluble in benzene. The ^{1}H NMR spectra of **4** and **5** are consistent with the cyclic and acyclic structures shown. In **4** the signals for the CH_2CH_2 ring hydrogens are split into two multiplets, one due to the two hydrogen atoms cis to the phenyl on the pyramidal phosphorus and the other due to the two hydrogen atoms trans to the phenyl. In **5**, these four hydrogens give rise to a singlet, as expected. Otherwise the spectral characterization of **4** and **5** is straightforward.

Synthesis of Tungsten Adducts. Preparation of the tungsten pentacarbonyl adduct of **4** is conveniently carried out on a 1-g scale by reaction with $(THF)W(CO)_5$[22] to give **6** in 77% yield as a white powder (Scheme 2). Coordination of **4** to tungsten via the phosphorus atom is clear on the basis of the observed chemical shifts and the tungsten−phosphorus satellites (due to the 14% natural abundance of ^{183}W) in the ^{31}P NMR (**4**, 91.3 ppm; **6**, 122.1 ppm, $^{1}J_{PW} = 329$ Hz) and phosphorus-carbon coupling in the ^{13}C NMR spectrum ($J_{PC} = 37$ and 8 Hz for the trans and cis carbonyl ligands, respectively). In addition, a non-sulfonyl analog, $(Et_2N)_2PhPW(CO)_5$ (**7**), was prepared by the same route and found to exhibit NMR and IR spectra that were sufficiently comparable to conclude that the compounds are both P-ligated $LW(CO)_5$ adducts.

In order to prepare a chelated complex from **5**, reactions were carried out with *trans*-$BrW(CO)_4NO$,[19,20] since the resultant adduct would be the precursor for the desired Lewis acid Diels−Alder catalyst.[20] Using our standard method (30 min reflux in THF)[20] or letting the reactants stand in $CHCl_3$ for 1 day gave a high yield of the desired complex **8** (Scheme 2). During the

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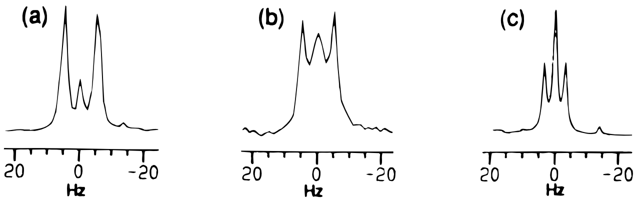

Figure 1. ^{13}C NMR spectra. The meta PPh carbon atoms provide representative AA′X ^{13}C NMR signals (A, A′ = ^{31}P, X = ^{13}C), illustrating the effect of J_{PP} ($J_{P'C} \approx 0$ Hz): (a) **9**, 129.03 ppm, $^3J_{PC}$ = 10.5 Hz, J_{PP} = 3 Hz; (b) **8**, 128.40 ppm, $^3J_{PC}$ = 9.7 Hz, $J_{PP} \approx 5$ Hz; (c) diphos, 128.44, $^3J_{PC}$ = 6.4 Hz, J_{PP} = 35 Hz.

course of this work it was found that if **5** was contaminated with any $Et_3NH^+Cl^-$ remaining from its synthesis, the reaction with $BrW(CO)_4NO$ gave a new compound that is spectroscopically similar to **8** and presumed to be the chloride analog. The facility of this side-reaction is unexpected and these results will be reported separately.[23] The known $Ph_2PCH_2CH_2PPh_2$ (diphos) adduct (**9**) was prepared for comparison to **8**,[24] as was adduct **10** of the electron-withdrawing diphosphine ligand $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$ (diphos-F_{20}). Unfortunately **10** was too insoluble to acquire a ^{13}C NMR spectrum, although the IR, ^{1}H, and ^{31}P NMR spectral features are comparable to those of **8** and **9**.

The IR and NMR spectra of **8** are similar to those of known chelate nitrosyl bromide analogs[20,24] and so it is presumed to be isostructural. Each of **8**, **9**, and **10** exhibit two carbonyl bands and a nitrosyl band in the IR, although **8** reproducibly exhibits a small splitting of this band (~4 cm^{-1}) suggestive of two conformational isomers either due to the 7-member chelate ring or more likely due to rotation about the N−S bonds of the tosyl moieties. In addition, **10** exhibits bands at 1522 and 1483 cm^{-1} that are even stronger than the carbonyl and nitrosyl bands, but these are assigned to C_6F_5 ring modes since they are virtually unchanged from bands observed in the IR spectrum of the free ligand. The molecular symmetry of **8** is confirmed by the fact that **8** and **9** each exhibit a singlet in their ^{31}P NMR spectrum while **10** exhibits a single fluorine-coupled multiplet, each with the expected ^{183}W satellites; furthermore, each of **8**−**10** exhibits two multiplets in the ^{1}H NMR spectrum for the two pairs of chelate backbone hydrogens that are syn to the NO and Br ligands, respectively. In addition, **8** exhibits a single tosyl methyl singlet, so if there is any conformational isomerism involving the relative orientations of the tolyl moieties, it is fast on the ^{1}H NMR time scale. The ^{13}C NMR spectra of **8** and **9** similarly conform to the proposed symmetry, with a single signal for the chelate backbone carbon and two sets of signals for the phenyl carbons (two phenyl rings syn to NO, two to Br) and for **8** a single set of tolyl carbons, again indicating the absence of conformational differences on the NMR time scale.

Simulation of the ^{13}C NMR Spectra. While the number of signals in the ^{13}C NMR spectra were consistent with the proposed structures, the individual signals merit scrutiny, since many exhibit additional lines due to "virtual coupling" to the distant phosphorus atom (Table 1, Figure 1). Each ^{13}C nucleus is nominally part of an AA′X system where the ^{13}C X nucleus is coupled to the magnetically inequivalent AA′ phosphorus nuclei. The observed multiplets will depend on the sign and relative magnitudes of $^2J_{PP}$ (coupling though tungsten), $^3J_{PP}$ or $^5J_{PP}$ (coupling through the chelate backbone for **9** and **8** respectively), and the various carbon−phosphorus coupling constants.[25] Simulated spectra have been published for a variety of combinations of coupling constants.[26−28] For **8** and **9**, the signals with $J_{PC} \approx 6{-}20$ Hz all give three-line signals, where the separation of the two outer lines is equal to $|J_{PC} + J_{P'C}|$; since in most cases the longer range coupling is zero, the separation of the outer lines is equal in magnitude to J_{PC}. The height of the middle line depends on the relative size of J_{PP}, allowing its magnitude to be approximated by simulation of the observed spectrum. The multiplets with $J_{PC} \approx 40{-}50$ Hz would not be expected to yield a detectable central line in the multiplet. Simulations of the observed multiplets were carried out, and while no attempt was made to carry out a completely rigorous analysis, coupling contstants for **8** and **9** that can generate the observed multiplets were found with $J_{PP} \approx 5$ Hz for **8** and 3 Hz for **9**. Representative NMR signals are shown in Figure 1, illustrating the dependence of the appearance of these multiplets on J_{PP}. The value for **9** is consistent with a literature value of 5.5 Hz for (diphos)$W(CO)_4$.[25] The value for **8** might be compared to values[25] of −15.0 Hz for a complex with a 7-member chelate ring, $(Ph_2P(CH_2)_4PPh_2)W(CO)_4$, and of 2.9 Hz for a complex with P−N bonds in the chelating ligand, $(Ph_2P(NH)PPh_2)W(CO)_4$, but no conclusions can be drawn from these particular numbers.

The ^{13}C NMR spectra of diTosL and diphos were recorded as well. The spectrum of diTosL apparently is first-order because $^5J_{PP} = 0$, but the complete absence of visible phosphorus coupling to the backbone CH_2 (i.e. $^2J_{PC} = {}^3J_{PC} = 0$) is unexpected. An alternative explanation is that $|J_{PC} + J_{P'C}| = 0$, where $^2J_{PC} = -{}^3J_{PC}$. This equality is nearly reached in diphos (*vide infra*), so this possibility cannot be dismissed, and in fact other workers have reached this conclusion previously.[28,29]

The 100 MHz ^{13}C NMR spectrum of diphos was consistent with that previously reported at 25 MHz,[29] but could not be simulated as an AA′X spin-system. In particular, the center line of the putative AA′X CH_2 multiplet is split by 2.5 Hz, and the pattern is readily modeled as an ABX system with $\Delta\nu_{PP'}$ = 3 Hz; the chemical shift equivalency of the phosphorus atoms is broken by the proximity of one to ^{13}C and the other to ^{12}C. The backbone CH_2 groups of **9** also exhibit such splitting of what in this case is a weak central line, and in general the spectra for **8** and **9** were better fit using $\Delta\nu_{PP'} = 1{-}3$ Hz. Other workers have commented on the possibility that the rigorously ABX nature of this type of spin-system can affect the observed spectrum,[28−31] but examples that necessitate the ABX formulation, including $(\eta^3\text{-2-methylallyl})_2Ru(PMe_3)_2$, *trans*-$(MeO)_2P(O)CH{=}CHP(O)(OMe)_2$, $Ph(H)PCH_2CH_2P(H)Ph$, and some $Ph_2P(CH_2)_3PPh_2$ platinum complexes, are rare.[32−35] The likely

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Table 3. Carbonyl Stretching Frequencies, Force Constants,[42] and σ and π-Bonding Parameters[38] for $LW(CO)_5$ Complexes[a]

L	ν(CO) cm^{-1}			F_{CO} (md/Å)				
	A_1^2 (w)	A_1^1 (m)	E (s)	k_1	k_2	k_i	Δd	$\Delta\pi$
$PPh(NEt_2)_2$	2069.6	1941.7	1935.9	15.46	15.78	0.32	−0.1346	0.1789
PPh_3	2071.2	1942.0	1942.0	15.45	15.87	0.31	−0.0131	0.1583
$P(OMe)_3$	2078.9	1962.2	1947.8	15.79	15.96	0.32	−0.0934	0.3324
TosL (**4**)[b]	2081.1	1960.0	1958.4	15.72	16.10	0.30	0.0787	0.2967
$P(CF_3)_3$[c]	2101	2006	1998	16.38	16.53	0.27	0.1848	0.6268

[a] Solvent is hexane except as noted. [b] ν(CO) in CH_2Cl_2: 2079.9 (w, A_1^2), 1992.6 (w, shoulder, B_1) 1951.6 cm^{-1} (s, overlapping A_1^1 and E), giving $k_1 = 15.59$, $k_2 = 16.03$, and $k_i = 0.31$ mdyn/Å. The IR in hexane was taken by FT-IR with nitrogen purging of the sample chamber, acquiring 250 scans at 1 cm^{-1} resolution. The saturation solution (baseline at 99.90% transmittance (%T) with a noise level of ±0.03 %T) gave for the A_1^2 band an intensity of 99.7 %T and for the overlapping A_1^1 and E bands an intensity of 98.4 %T. [c] Cyclohexane solution.[18]

reason for our observation, at least in the case of diphos, is the higher field-strength used (400 MHz for ^1H), due not to the higher dispersion in the ^{13}C NMR where the observed splittings are merely due to spin-spin coupling, but rather to the higher dispersion in the ^{31}P NMR, since this will increase $\Delta\nu_{PP'}$. These results will be described in detail elsewhere.[36]

Infrared Spectra. Ligand σ-donor and π-acid strength is most simply assessed by infrared CO stretching frequencies.[37−39] While the separation of these effects by IR has been questioned,[40,41] comparisons that involve a constant donor atom (here phosphorus) may be made with relative confidence. Infrared data, calculated Cotton−Kraihanzel CO force constants,[42] and derived parameters are collected in Table 3 for $W(CO)_5$ adducts of several phosphorus ligands including **4**. Consideration of the CO stretching frequencies themselves or the trans and cis CO stretching force constants k_1 and k_2 clearly shows that while **4** is not as good a π-acceptor nor as poor a σ-donor as $P(CF_3)_3$, it is somewhat comparable to $P(OMe)_3$ despite the presence of the phenyl group in place of a third heteroatom. Consideration of Dobson's Δd and $\Delta\pi$ parameters[38] suggests than **4** is comparable in π-acceptor ability to $P(OMe)_3$ but is a much weaker σ-donor. The effect of the sulfonyl groups is enormous, since $PPh(NEt_2)_2$ is a much stronger σ-donor and weaker π-acceptor than **4**. The data suggests a relative ordering of ligand acceptor ability of $P(CF_3)_3 >$ **4** $\approx P(OMe)_3 > PPh_3 \approx PPh(NEt_2)_2$, and of ligand donor ability of $PPh(NEt_2)_2 \geq P(OMe)_3 > PPh_3 >$ **4** $> P(CF_3)_3$. On the basis of the IR data, the *N*-sulfonylphosphoramide ligand is second only to fluorinated phosphines in electron-deficiency.

A smaller set of data was collected for comparison of the diTosL (**5**) and $Ar_2PCH_2CH_2PAr_2$ (Ar = Ph, C_6F_5) ligands using the nitrosyl bromide adducts **8**−**10** as well as the analogous bis(acetonitrile) adduct[43] *cis,cis,trans*-$(CH_3CN)_2(CO)_2(NO)WBr$ (Table 4). As before Cotton−Kraihanzel force constants were calculated,[44] but no attempt was made to compare σ and π effects for this limited data set. The data show that the electron-withdrawing diTosL and fluorinated ligands are qualitatively quite different from the stronger donor diphos and acetonitrile ligands; **8** actually exhibits the highest ν(NO) and k_{NO} of the group. What makes this particularly interesting is that the substitution of *two* perfluorophenyl groups for the phenyl rings of diphos has a comparable effect to substitution of *one* sulfonamide for the CH_2 linker of diphos. Once again, the IR data suggest that the sulfonyl moiety is quite an effective electron-withdrawing group.

Table 4. Carbonyl and Nitrosyl Stretching Frequencies and Force Constants[44] for *cis*-$L_2W(CO)_2(NO)(Br)$ Complexes[a]

L_2[b]	ν(CO) cm^{-1}		ν(NO) cm^{-1}	$F_{CO/NO}$ (md/Å)		
	A^2 (m)	B (m)	A^1 (m)	k_{NO}	k_{CO}	k_i
$(CH_3CN)_2$[c]	2015	1930	1630	11.82	15.66	0.62
diphos	2025.8	1954.4	1630.0	11.78	15.96	0.53
diTosL (**5**)	2035.0	1966.6	1652.4[d]	12.11	16.14	0.51
diphos-F_{20}	2055.3	1994.4	1649.2	12.03	16.54	0.46

[a] Solvent is benzene except as noted. [b] Diphos and diphos-F_{20} = $Ar_2PCH_2CH_2PAr_2$ (Ar = Ph and C_6F_5, respectively). [c] Solvent is CH_2Cl_2.[43] [d] Average of reproducibly observed splitting of peak (1654.1, 1650.8 cm^{-1}).

NMR Spectra. Numerous groups have attempted to correlate electronic properties of ligands with their NMR chemical shifts and/or coupling constants,[39,45−49] but it is fair to say that none of the results have led to the type of widespread use enjoyed by the above IR methods. For phosphorus tungsten pentacarbonyl complexes, there appears to be a positive correlation between $^1J_{PW}$ and the electron-withdrawing ability of the ligand.[45,46,50,51] In order to determine whether or not the NMR data for the *N*-sulfonylphosphoramide ligands fits this correlation and/or is unusual, ^{13}C and ^{31}P NMR spectra were collected for PPh_3, $PPh(NEt_2)_2$, $P(OMe)_3$, and their $W(CO)_5$ adducts for comparison to those of **4** and **6**, along with data for the chelating phosphines (Tables 1, 2).

The order of $^1J_{PW}$ increases as $PMe_3 < PPh_3 < PPh(NEt_2)_2 < P(CF_3)_3 <$ TosL $< P(OMe)_3$, and for the chelating ligands as diphos < diphos-F_{20} < diTosL, again supporting the notion that the phosphoramides are highly electron-withdrawing, although the precise ordering on this basis is suspect. The change in phosphorus chemical shift upon coordination, $\Delta\delta_P$, varies from −0.6 ppm for $P(OMe)_3$ to +57.9 ppm for $P(CF_3)_3$, and does not appear to be of any utility. For instance, $P(OMe)_3$ and $P(CF_3)_3$ are both electron-withdrawing ligands (on the IR scale) and both exhibit large tungsten−phosphorus coupling constants of 386 and 300 Hz, respectively, yet their $\Delta\delta_P$ values fall at the two extremes. Of the remaining ligands, data for all except $PPh(NEt_2)_2$ (for which $\Delta\delta_P = +7.7$) fall in the relatively narrow range of 24 ± 7 ppm after one takes account of the well-documented "ring contribution" ΔR for chelating phos-

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phines.[52] That is, five-member chelate rings typically are deshielded by ∼30 ppm compared to the related nonchelated adducts; for instance ΔR for (diphos)W$(CO)_4$ is +27.3 ppm. The limited data available for larger rings suggests that $\Delta R = 0$ for the seven-member ring of **8**. After this adjustment, then, all three of the chelating adducts would have $\Delta\delta_P$ values near +20 ppm.

In the ^{13}C NMR, $^2J_{PC}$ for the trans carbonyl ligand (22, 26, 37, and 38 Hz, respectively for PPh_3, $PPh(NEt_2)_2$, **4**, and $P(OMe)_3$) follows the same pattern as $^1J_{PW}$ ($^2J_{PC}$ for the cis-CO's follows the same trend but lies in a range from 7.3 to 10.9 Hz). A unique feature of this set of phosphines is the presence of the phenyl group on phosphorus, so in addition to the comparisons of $^1J_{PW}$ obtained from the ^{31}P NMR, comparisons of phenyl coupling constant and chemical shift data obtained from the ^{13}C NMR can be made. Another unique feature is that in all cases for the nonchelating set, *the ^{13}C NMR spectra were measured at 50 and 100 MHz, so assignments involving doublets due to coupling to phosphorus are unambiguous*. While the chemical shifts do not change much from compound to compound or upon complexation, coupling constants of the phosphorus−phenyl carbons do vary although at this point the differences are better described as a curiosity than an illuminating point of comparison. Thus, PPh_3 exhibits an increase in the one-bond $P-C_{ipso}$ coupling constant (ΔJ_{ipso}) of 31 Hz upon coordination (from 10.7 to 41.6 Hz), while **4** exhibits a *decrease* of 12 Hz (from 32.1 to 20.1 Hz). While $PPh(NEt_2)_2$ exhibits an increase like PPh_3, the actual values are quite different, namely a 67 Hz increase from 3.4 to 70.2 Hz. The chelating ligands exhibit ΔJ_{ipso} values (26 and 29 Hz for **8** and **9**) that are similar to that of PPh_3, so TosL is anomalous in the sign and $PPh(NEt_2)_2$ in the magnitude of ΔJ_{ipso}.

An obvious question is whether or not $PPh(NEt_2)_2$ is an appropriate model compound for TosL. We chose not to examine the more appropriate cyclic analog, 1,3-dimethyl-2-phenyl-1,3,2-diazaphospholidine (i.e. the analog of TosL in which the tosyl moieties are replaced by methyls), because of a warning about acute nausea and vomiting caused by several related cyclic compounds.[11] In fact, $^1J_{PC}$ for $PPh(NEt_2)_2$ has been reported to vary with temperature, rising from 0 Hz in the 20−45 °C range to 2 Hz at 85 °C (we have no explanation for the discrepancy between these values and our room-temperature value of 3.4 Hz; the chemical shifts are comparable). In contrast, in 1,3-dimethyl-2-phenyl-1,3,2-diazaphospholidine, $^1J_{PC} = 42$ Hz and is temperature independent.[53] The temperature effect was proposed to be due to rotation about the P−N bonds, while the large disparity in coupling constants despite the near-identity of attached atoms was presumed to be due to hybridization changes at phosphorus as well as fixing the P−N lone pair dihedral angles. This would suggest that for $PPh(NEt_2)_2$ the steric and electronic consequences of coordination to tungsten are simply larger than for the other compounds, while the cyclic TosL ligand perhaps undergoes a somewhat different hybridization change upon coordination than do the other (acyclic) compounds.

Further close inspection of the data reveals other curious points—for instance $^2J_{PC}$ is larger than $^1J_{PC}$ for free PPh_3, $PPh(NEt_2)_2$, diphos, and diTosL, but smaller for TosL and all of the complexed ligands. One-bond phosphorus−carbon coupling constants in particular are well-known to be quite variable,[54] so this switching in absolute magnitude of one- and two-bond coupling constants is not unusual. This comparison depends on the validity of the assignments of the ortho and meta phenyl carbons, but phosphorus coupling to ortho and meta phenyl carbons is known to follow the order $^2J_{PC} > {}^3J_{PC}$.[54] Further confidence in the ortho/meta assignments arises from the internal consistency of the chemical shift data: all of the ortho carbons are downfield of the meta carbons. Nonetheless, the limited data set does not permit further generalizations.

Conclusions

The demonstration of the ease of synthesis of TosL and diTosL, the first arylsulfonylphosphoramide ligands, opens up a variety of research opportunities. The IR and to a lesser extent the NMR data suggest that the sulfonamide moiety is strongly electron-withdrawing in character, on a par with perfluorinated alkyl groups. Work in progress includes the use of these ligands in tungsten nitrosyl Diels−Alder catalysts and the synthesis of chiral analogs[55] that may allow catalytic asymmetric induction of Diels−Alder reactions.

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