Articles

Sterically Tunable Phosphenium Cations: Synthesis and Characterization of Bis(arylamino)phosphenium Ions, Phosphinophosphenium Adducts, and the First Well-Defined Rhodium Phosphenium Complexes

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A family of bis(arylamino)chlorophosphines of the general formula Cl[PN(Ar)CH_2CH_2N(Ar)] (Ar = 4-MeO-C_6H_4, **3a**; Ar = 2,4,6-Me_3-C_6H_2, **3b**; Ar = 2,6-$(CHMe_2)_2$-C_6H_3, **3c**) has been prepared from PCl_3 and the appropriate diamine. Steric interactions involving the 2,6-aryl substituents in **3b**,**c** result in hindered rotation about the N−C_{Ar} bond, as evidenced by ^{1}H NMR spectroscopy. Treatment of halophosphines **3a**−**c** with $AgOSO_2CF_3$ (AgOTf) or Tl{B[3,5-$(CF_3)_2$-C_6H_3]$_4$} ($TlBAr_F$) affords the cationic bis(arylamino)phosphenium compounds [PN(Ar)CH_2CH_2N(Ar)](A), (**4a**−**e**; A = OTf, BAr_F), in high yield. Phosphenium cations **4a**−**d** reversibly form adducts with trimethylphosphine. The structure of the phosphinophosphenium adduct **5c** (Ar = 2,6-$(CHMe_2)_2$-C_6H_3) has been determined by single-crystal X-ray diffraction techniques, revealing both the steric influences of the 2,6-Ar substituents and the electronic nature of the bonding in **5**. Treatment of Wilkinson's catalyst, $RhCl(PPh_3)_3$, with 1 equiv of **4a** gives the first well-defined Rh phosphenium complex, {*trans*-$RhCl(PPh_3)_2$-[PN(4-MeO-C_6H_4)CH_2CH_2N(4-MeO-C_6H_4)]}(OTf) (**6**), which is isolated in 80% yield. In contrast, treatment of Wilkinson's catalyst with **4c** results in quantitative formation of [Rh(PPh_3)$_3$](OTf) and chlorophosphine **3c**. The influence of the phosphenium N−Ar substituents is further evidenced by the analogous reaction between $RhCl(PPh_3)_3$ and mesityl-substituted **4b**, which affords products analogous to **4a**,**c** as well as the isomeric Rh phosphenium complex **7a**, having *cis* PPh_3 ligands. ^{31}P NMR spectroscopic parameters for **6** and **7a**,**b** are consistent with Rh−P multiple bonding.

Introduction

Significant advances in the use of electrophilic late-metal complexes as homogeneous catalysts have been realized in the last 5 years. In particular, cationic group 10 species of general formula $[L_nMR]^+$ have been successfully employed for the selective functionalization of alkanes[1−3] and for polymerization,[4] copolymerization,[4,5] and functionalization[6] of unsaturated hydrocarbons. Common to many of the catalysts employed for these reactions are two general features: (1) the transition-metal complexes that satisfy the electronic requirements for reactivity are generated by protonation of an alkyl group or abstraction of a halide or alkyl group from neutral L_nMR_2 or L_nMX_2 precursors and (2) control over the steric environment at the metal center, through use of the appropriate ligand ensemble, is invaluable for obtaining high catalyst activity.

It occurred to us that utilization of cationic phosphenium ligands of the general formula [PN(Ar)CH_2CH_2N(Ar)](A) (Ar = substituted aryl group, A = weakly coordinating/noncoordinating counterion) could offer additional methods (i.e., addition or substitution) for synthesizing late-metal electrophiles in which steric and electronic environments could be easily controlled (Scheme 1). In addition, the availability of multiple metallophosphenium resonance structures may provide additional means of stabilizing reactive organometallic species (Scheme 2).

The coordination chemistry of cationic phosphenium ions, $[PR_2]^+$, has been developed extensively since the

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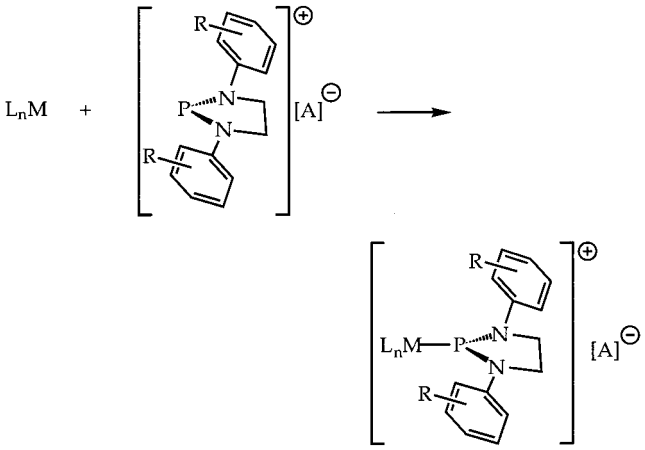
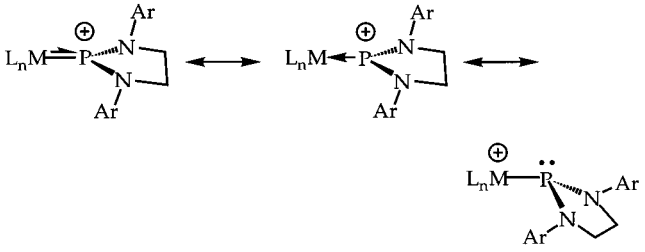
Scheme 1



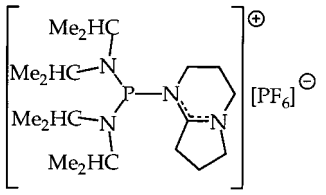
Scheme 2



initial report of a dicoordinate phosphorus cation over 35 years ago.[7] Ligation of one or more heteroatoms to the electrophilic phosphorus center has facilitated the synthesis of a wide variety of stable phosphenium salts, phosphenium-donor adducts, and metallophosphenium complexes. Phosphenium cations may be both σ-donors and π-acceptors, rendering them isoelectronic with neutral carbene, silylene, and carbon monoxide fragments.[8,9] The free cationic phosphenium ligands, which typically incorporate hydrocarbon, aryloxy, or alkylamino groups covalently bound to phosphorus, form adducts with a variety of neutral bases, permitting the characterization of both amino-[10−12] and phosphinophosphenium[11,13−18] complexes.

For phosphenium−phosphine adducts, ^{31}P NMR spectroscopy is invaluable for probing the extent of P−P interaction; $^{1}J_{P-P}$ coupling constants typically fall in the range of 240−385 Hz, both for compounds in which the phosphine is covalently attached to one or both of the R substituents and for adducts which do not contain such a chelating tether.[11,13−19] Shagvaleev and co-workers investigated phosphinophosphenium compounds of the general formula [RXP−PRXCl][A] (R, X = −Cl, $-C_2H_5$, $-C_6H_5$, −4-Cl-C_6H_4, −4-CH_3-C_6H_4; A = $AlCl_4$, Al_2Cl_7, $AlClBr_3$, Al_2Br_6Cl) by variable-temperature ^{31}P NMR spectroscopy.[18] The ambient-temperature spectra of some of these salts exhibited broad resonances, indicative of rapid, reversible phosphine dissociation; typical AB spin systems were observed at low temperatures. These studies indicated that the lability of the P−P bond depends on both the chlorophosphine substituents and the aluminum counterion employed.

Examples of structurally characterized phosphenium-donor complexes are rare in comparison to the number of phosphenium-donor complexes that have been observed spectroscopically. X-ray diffraction studies of compounds in which neutral amines or phosphines are tethered to the phosphenium center have been reported by Schomburg,[20] Schmutzler,[21−23] Gololobov,[24] Lappert,[25] and Burford;[26] Reed and co-workers reported the first example of a structurally characterized phosphenium-donor complex in which the donor is not covalently attached to one of the phosphenium R substituents: namely, the DBU adduct of {[$(Me_2HC)_2N]_2P$}(PF_6) (**I**),[10]



(**I**)

in which the positive charge is delocalized over the two DBU nitrogens (DBU = (1,8-diazabicyclo[5.4.0]undec-7-ene). Burford and co-workers subsequently reported structures of two complexes in which amine moieties are intermolecularly coordinated to zwitterionic aluminatophosphines, $Cl_2Al(\mu$-$NSiMe_3)_2PNMe_2CH_2CH_2NMe_2$-$P(\mu$-$NSiMe_3)_2AlCl_2$ (**II**) and $Cl_2Al(\mu$-$NSiMe_3)_2PN(CH_2$-$CH_2)_3CH$ (**III**),[27] as well as disordered crystal structures of the phosphine−phosphenium−gallium chloride complex **IV**, $[Me_2ClPPMe_2GaCl_3][GaCl_4]$.[14,19] Although several examples of intermolecular phosphine coordination to low-coordinate cationic phosphorus centers (such as $R_2C{=}P^+$ and $ArP{=}P^+$ ions) have been reported,[28,29] **I**−**IV** represent the only structurally characterized intermolecular phosphenium-donor compounds to date.

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The use of phosphenium ions as ligands for transition metals has also been investigated, although primarily with group 6 and 8 metals. A variety of η^5-cyclopentadienyl (Cp) molybdenum[30−41] and tungsten[41,42] pianostool complexes, as well as a Cp-free complex of manganese,[43] have been prepared by treatment of neutral halophosphines with anionic transition-metal fragments, as shown in eq 1. A cationic, trigonal-bipyramidal iron−phosphenium complex,[44] cationic piano stool complexes of molybdenum,[45] tungsten,[45−48] iron,[49−53] and ruthenium,[54] and cationic octahedral complexes of chromium,[55−57] molybdenum,[55−58] and tungsten-[55−57] were all readily obtained from hydride, halide, or alkoxide abstraction from neutral M−phosphine or −phosphinite precursors (eq 2).

$$[L_nM]^- + X{-}PE_2 \rightarrow L_nM{-}PE_2 + X^- \qquad (1)$$

$$L_nM{-}PE_2R \xrightarrow[-R^-]{\text{Lewis acid}} [L_nM{-}PE_2]^+ \qquad (2)$$

Comparatively few reports exist in the literature of phosphenium compounds of group 9 or 10 transition metals. The only known group 10−phosphenium complexes are the structurally characterized zwitterion $Cl_2Ga(\mu\text{-}NSiMe_3)_2P{=}Ni(CO)_3$, reported by Niecke,[59] and the clusters $\{[(R_2N)_2P]Pd(\mu\text{-}Cl)\}_3$ (R = $CHMe_2$, C_6H_{11}), recently observed by Dyer.[60] Lang and co-workers reported neutral Co−phosphenium compounds of the general formula $(R)(R')P{=}Co(CO)_3$, which may be synthesized by the route shown in eq 2[42,61,62] (R = 2,4,6-$(CMe_3)_3$-C_6H_2O, R′ = CH=CHPh; R = 2,4,6-$(CMe_3)_3$-C_6H_2O, R′ = C_5Me_5; R = 2,4,6-$(CMe_3)_3$-C_6H_2O, R′ = (η^2-CCPh)$Co_2(CO)_6$) or by reductive dehalogenation of (R)(R′)PCl by $Co_2(CO)_8$ (R = 2,6-$(CMe_3)_2$-4-Me-C_6H_2O, R′ = (η^2-CCPh)$Co_2(CO)_6$; R = 2,4,6-$(CMe_3)_3$-C_6H_2O, R′ = (η^2-CCPh)$Co_2(CO)_6$).[63,64] A recent report by Breit[65] indicated that regioselectivity for internal aldehyde in sytrene hydroformylation was increased by addition of varying amounts of either $[P(NEt_2)_2](OTf)$ or {P[CH(Me)Ph]CH_2CH_2N[CH(Me)Ph]}(OTf) to $Rh(CO)_2(acac)$. Neither the organometallic complexes initially formed nor the catalytically active species operating in these systems could be identified.[66]

We report herein (1) the synthesis and characterization of a family of bis(arylamino)phosphenium compounds in which the aryl substituents may be varied in order to influence the steric environment at the phosphorus center, (2) assessment of the barriers to N−Ar rotation for bis(arylamino)chlorophosphines, (3) NMR spectroscopic characterization of reversible phosphino-phosphenium adduct formation, (4) the first structurally characterized intermolecular phosphine adduct of a bis(amino)phosphenium ion, and (5) the first well-defined, cationic group 9 phosphenium compounds, accessible in high yield from the addition of isolable phosphenium ions to a neutral Rh complex.

Results and Discussion

Synthesis and Characterization of Halophosphines and Phosphenium Ions. The synthetic route to bis(arylamino)phosphenium compounds **4** is shown in Figure 1. Treatment of glyoxal with 2 equiv of primary aromatic amine afforded bis(imines) **1a**−**c**[67−69] as bright yellow crystalline solids in good yield (69−84%). Sodium borohydride reduction of **1a**−**c**, followed by quenching with water, provided bis(amines) **2a**−**c**[70,71] in 77−87% yield; although **2a**−**c** are known compounds, the synthesis described above provides considerable

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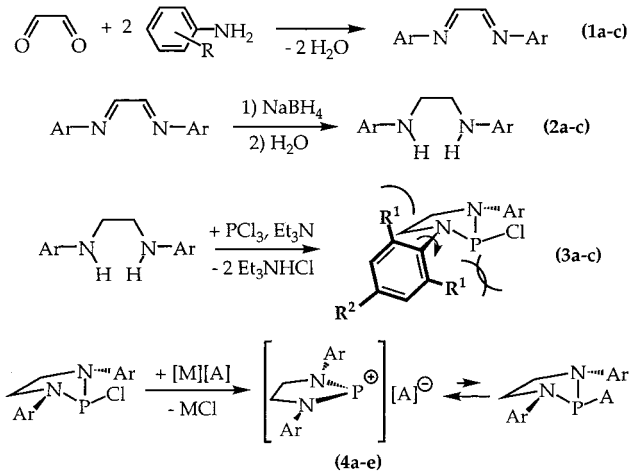


Figure 1. Syntheses of bis(arylamino)phosphenium complexes. [M][A] = $AgOSO_2CF_3$, $TlB[3,5\text{-}(CF_3)_2\text{-}C_6H_3]_4$. **1a**−**3a**: Ar = 4-MeO-C_6H_4. **1b**−**3b**, Ar = 2,4,6-Me_3-C_6H_2. **1c**−**3c**, Ar = 2,6-$(CHMe_2)_2$-C_6H_3. **4a**, Ar = 4-MeO-C_6H_4, [A] = OSO_2CF_3. **4b**: Ar = 2,4,6-Me_3-C_6H_2, [A] = OSO_2CF_3. **4c**: Ar = 2,6-$(CHMe_2)_2$-C_6H_3, [A] = OSO_2CF_3. **4d**: Ar = 4-MeO-C_6H_4, [A] = $B[3,5\text{-}(CF_3)_2\text{-}C_6H_3]_4$. **4e**: Ar = 2,4,6-$Me_3$-$C_6H_2$, [A] = $B[3,5\text{-}(CF_3)_2\text{-}C_6H_3]_4$.

improvement in isolated yield relative to previously reported procedures. Chlorophosphines **3a**−**c** were isolated as moisture-sensitive Et_2O- or THF-soluble solids from the treatment of CH_2Cl_2/triethylamine solutions of the appropriate diamine with 1 equiv of PCl_3.

The steric effects of the N−Ar groups are evident upon examination of the NMR spectra of **3a**−**c**, as Ar···Cl interactions may inhibit rotation about the $N-C_{Ar}$ bond. Whereas complex **3a**, with relatively uncongested 4-MeO-C_6H_4 groups, exhibits unrestricted rotation about the $N-C_{Ar}$ bonds, even at temperatures as low as −58 °C, mesityl-substituted chlorophosphine **3b** exhibits temperature-dependent NMR spectra. The two *ortho* methyl resonances observed at δ 2.21 and 2.61 in the ^{1}H NMR at −69 °C give rise to a sharp singlet at δ 2.39 at 98 °C, corresponding to a free energy of activation $\Delta G^{\ddagger}$ of 15.4 (± 0.1) kcal/mol (T_c = 50 °C, toluene-d_8). The peak separations for both the *ortho* methyls and *meta* hydrogens do not reach an invariant value at low temperatures, thus precluding deconvolution of $\Delta G^{\ddagger}$ into enthalpic and entropic terms.

Incorporation of bulky isopropyl groups in the 2- and 6-aryl positions completely inhibits rotation about the $N-C_{Ar}$ bonds, as evidenced by two sets of observed resonances for the pairwise-inequivalent $CHMe_2$ groups in the ^{1}H NMR spectra of **3c**. As shown in Figure 2a, the resonances for the two magnetically inequivalent isopropyl methine hydrogens are observed at δ 3.38 and 3.84. The corresponding isopropyl methyl resonances are observed as a series of overlapping doublets (inset, Figure 2a); selective decoupling experiments confirmed that the six-line pattern centered at δ 1.32 is, in fact, four overlapping doublets (δ 1.29, J = 7.3 Hz; δ 1.31, J = 7.3 Hz; δ 1.32, J = 6.8 Hz; δ 1.35, J = 6.4 Hz). No coalescence or broadening of the observed NMR signals is observed, even at 100 °C (toluene-d_8). A lower limit of 17.7 kcal/mol for the barrier to N−Ar rotation may be inferred from the 138 Hz peak separation of the C*H*Me_2 resonances in **3c**. The possibility of **3c** existing as a 1:1 mixture of two distinct geometric isomers with coincidentally equivalent ^{31}P NMR resonances is eliminated on the basis of the observed $^{13}C\{^1H\}$ NMR spectrum, which shows a *single* resonance for the heterocycle N*C*H_2 carbons (54.76 ppm, $^2J_{P-C}$ = 10 Hz).

Table 1. $^{31}P\{^1H\}$ NMR Data for 3−5

compd	solvent	temp (°C)	$\delta(P(NRAr)_2)$ (ppm)	$\delta(PMe_3)$ (ppm)	$^1J_{P-P}$ (Hz)
3a	$CDCl_3$	25	138.7		
3b	$CDCl_3$	25	155		
3c	$CDCl_3$	25	154		
4a	$CDCl_3$	25	196.8		
4b	$CDCl_3$	25	203.1		
4c	$CDCl_3$	25	199.4		
4d	$CDCl_3$	25	225		
4e	$CDCl_3$	25	257		
5a	CD_2Cl_2	−90	105.0	7.6	442
5b	CD_2Cl_2	−90	127.4	−4.2	493
5c	CD_2Cl_2	−90	138.5	−6.0	504
5d	CD_2Cl_2	−90	134.5	−9.2	507

Alternative dynamic processes which could account for the observed chlorophosphine NMR spectra, including ring flippage of the five-membered heterocycle,[72] racemization of the configuration at a cationic P center resulting from P−Cl heterolysis,[10,73] inversion at N,[74] or inversion at P, are inconsistent with the observed combinations of spectral changes and associated kinetic parameters.

Treatment of the appropriate chlorophosphine with 1 equiv of $AgOSO_2CF_3$ (AgOTf) gives stable cationic bis(arylamino)phosphenium ions **4**, as evidenced by the 44−48 ppm downfield shifts of the ^{31}P NMR resonances for **4a**−**c**, relative to those for **3a**−**c** (Table 1). To probe the nature of cation−anion interactions, compounds **4d**,**e**, containing the weakly coordinating anion $\{B[3,5\text{-}(CF_3)_2\text{-}C_6H_3]_4\}^-$ (BAr_F), have been prepared by treatment of **3a**,**b** with 1 equiv of $TlBAr_F$. The fact that the [BAr_F] compounds exhibit ^{31}P NMR signals significantly deshielded (29−54 ppm) relative to the corresponding [OTf] compounds is indicative of a weakly coordinated triflate anion in **4a**−**c**, consistent with the solution phosphenium−triflate interactions observed previously by Kee and co-workers.[13]

Assessing the ease of N−Ar rotation for cationic phosphenium compounds **4a**−**c** is more difficult than for the corresponding halophosphines, due to the rapid, reversible binding of the triflate counterion. Two-coordinate cationic phosphenium compounds are generally considered to be planar (thus resulting in magnetically equivalent aryl substituents for compounds **4a**−**c**);[75] coordination of the triflate counterion to phosphorus would produce a pyramidal phosphorus center and, thus, inequivalent Ar substituents in the limit of slow N−Ar rotation. Although the upfield ^{31}P NMR chemical shifts of the triflate compounds relative to the corresponding borate compounds indicate some coordination of the triflate anion to the phosphorus center, both ^{1}H and ^{13}C NMR spectroscopy show magnetically equivalent aryl substituents for **4a**−**c** (even at temperatures as low as −35 °C); the ^{1}H NMR spectrum of **4c** at 25 °C is shown in Figure 2b. In accounting for the observed

(72) Oki, M. *Applications of Dynamic NMR Spectroscopy to Organic Chemistry*; VCH: Deerfield Beach, FL, 1985.
(73) Lamande, L.; Munoz, A. *Tetrahedron Lett.* **1991**, *32*, 75.
(74) Lehn, J. M.; Wagner, J. *Tetrahedron* **1970**, *26*, 4227.
(75) In the limit of slow $N-C_{Ar}$ bond rotation, we also assume that the N-aryl planes are eclipsed along the N−N axis (i.e. C_{2v} symmetry).

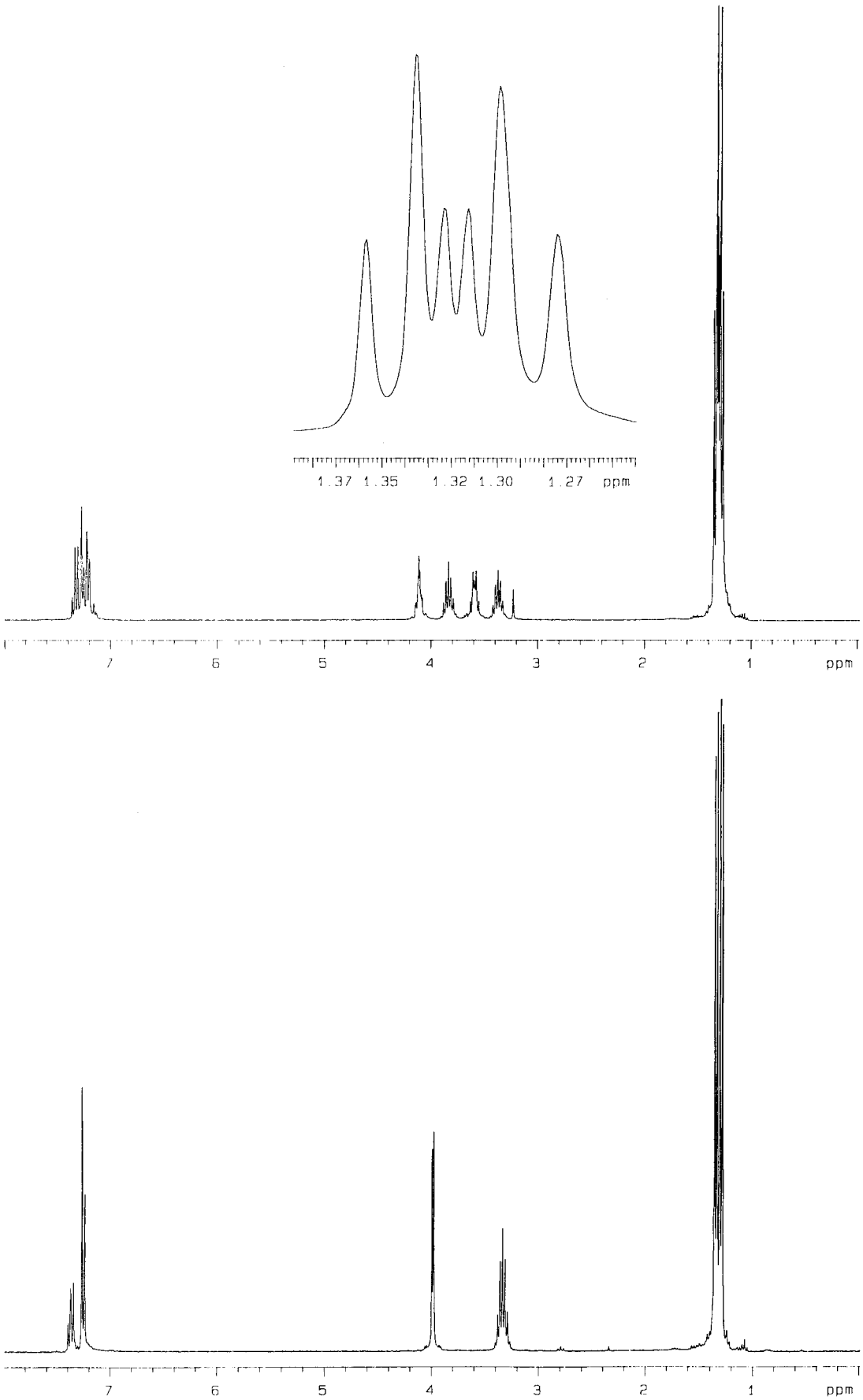


Figure 2. 300 MHz ^{1}H NMR spectra ($CDCl_3$) of (a, top) ClPN[2,6-$(CHMe_2)_2$-C_6H_3]CH_2CH_2N[2,6-$(CHMe_2)_2$-C_6H_3] (**3c**) (inset shows detail of overlapping $CHMe_2$ methyl resonances), (b, bottom) {PN[2,6$(CHMe_2)_2$-C_6H_3]CH_2CH_2N[2,6-$(CHMe_2)_2$-C_6H_3]}-(OTf) (**4c**).

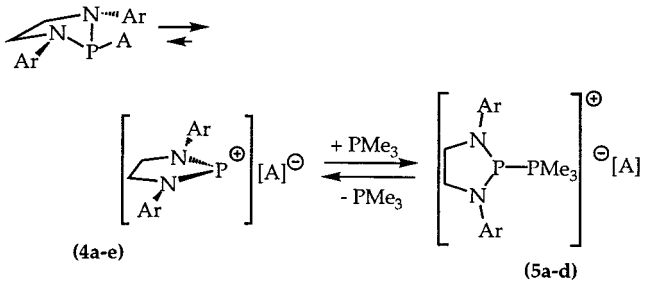
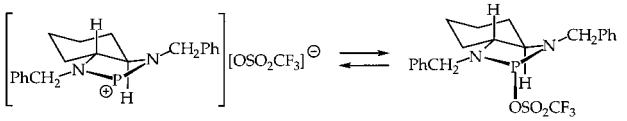


Figure 3. Equilibria between phosphenium and phosphinophosphenium complexes. **5a**: Ar = 4-MeO-C_6H_4, [A] = OSO_2CF_3. **5b**: Ar = 2,4,6-Me_3-C_6H_2, [A] = OSO_2CF_3. **5c**: Ar = 2,6-$(CHMe_2)_2$-C_6H_3, [A] = OSO_2CF_3. **5d**: Ar = 2,4,6-Me_3-C_6H_2, [A] = B[3,5-$(CF_3)_2$-C_6H_3]$_4$.

high symmetry of **4b**,**c**, we cannot differentiate between rapid rotation about the N−C_{Ar} bond and a dynamic equilibrium between covalently bound and discrete ionic triflate counterions, with the equilibrium weighted toward the planar, two-coordinate phosphenium complex.

For comparison, a previous crystal structure of the phosphenium−triflate complex **V**[13] revealed P−O bond distances of 2.841 and 2.755 Å, intermediate between the van der Waals distance for P−O interactions (3.35 Å) and P−O covalent single bond length (1.63 Å);[76] solution NMR studies ($CDCl_3$) on **V** indicate dynamic P−OTf interactions, with the "naked" phosphenium cation predominating at high dilution.



(V)

Synthesis and Characterization of Phosphinophosphenium Compounds. The electrophilic phosphenium compounds **4** reversibly form adducts with neutral bases, as exemplified by the formation of trimethylphosphine adducts **5a**−**d** (Figure 3). Despite the lability of the phosphine ligands at room temperature (vide infra), 1:1 phosphenium−phosphine adducts may be isolated by treatment of **4** with a slight excess of PMe_3 and then removal of volatiles in vacuo and/or filtration from toluene. At room temperature, the ^{31}P NMR resonances of **5a**−**d** are broad, indicating a rapid equilibrium between the free and bound species. At low temperatures, each of the phosphine and phosphenium peaks may be resolved into sharp doublets, with $^1J_{P-P}$ in the range of 442−507 Hz (Table 1). Of phosphinophosphenium adducts reported in the literature, only the chelating zwitterion[11] {[2,4,6-$(CMe_3)_3$-C_6H_2](AlCl$_3$)N}-[2-$(CH_2\overline{PPh_2})$-C_6H_4]P exhibits a higher $^1J_{P-P}$ value (525 Hz).

Inspection of the ^{31}P DNMR chemical shift data for **5a**,**b** (Figure 4) shows a gradual shift from the adduct toward the free phosphine and phosphenium cation; the loss of P−P coupling is observed above −30 °C. While we made no attempts to obtain equilibrium and rate constants, the most sterically congested phosphenium ion, **5c**, clearly forms the least stable adduct, as evidenced by the dramatic chemical shift changes toward free PMe_3 and phosphenium cation **4c** at temperatures above −20 °C. The observed rapid N−C_{Ar} rotation for **5c** (25 °C) is consistent with a labile phosphine ligand, as a bulky substituent ligated to the heterocycle phosphorus would be expected to result in slow N−C_{Ar} rotation (vide supra).

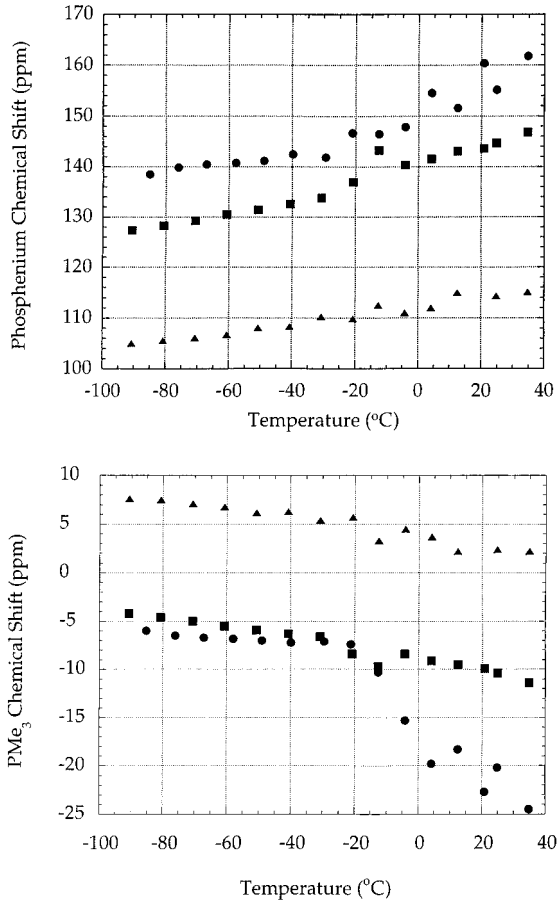


Figure 4. Variable-temperature ^{31}P NMR data (CD_2Cl_2) for phosphinophosphenium complexes **5a**−**c**: (a, top) phosphenium chemical shift versus temperature; (b) phosphine chemical shift versus temperature. Legend: (▲) **5a**; (■) **5b**; (●) **5c**.

Although a significant (7 ppm) downfield shift of the phosphenium ^{31}P NMR resonance was observed for **5d** (vs **5b**), no change in phosphine lability was observed upon switching from [OTf] to [BAr_F] counterions, in contrast to previous studies on aluminum halide salts of phosphinophosphenium adducts.[18]

Crystallographic Characterization of 5c. Single crystals of **5c** suitable for X-ray diffraction studies (Table 2) were grown at −15 °C from a 3:2 methylene chloride/diethyl ether solution. Although crystal structures have previously been obtained for several intramolecular phosphinophosphenium compounds, and structures with severe disorder were reported for the phosphinophosphenium-gallium trichloride complex **IV**, **5c** is the first well-behaved example of a structurally characterized *inter*molecular phosphinophosphenium adduct. A view of the phosphenium cation is shown in Figure 5, and selected bond lengths and angles are provided in Table 3.

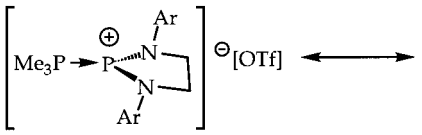
No cation−anion interactions are observed in the solid state for **5c**; the closest P−OTf distances are 3.432 Å

(76) Huheey, J. E. *Inorganic Chemistry: Principles of Structure and Reactivity*, 3rd ed.; Harper: New York, 1983.

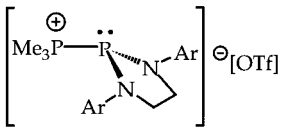
Table 2. Crystal Data and Structure Refinement for ([PMe$_3$]{PN[2,6-(CHMe$_2$)$_2$-C$_6$H$_3$]CH$_2$CH$_2$N-[2,6(CHMe$_2$)$_2$-C$_6$H$_3$]})(OTf) (5c)

empirical formula	$C_{30}H_{47}F_3N_2O_3P_2S$
fw	634.70
temp	203(2) K
wavelength	0.71073 Å
cryst syst	triclinic
space group	$P\bar{1}$
unit cell dimens	
a	10.4082(6)
b	10.7169(6)
c	16.1629(10)
α	99.956(1)
β	99.879(1)
γ	104.199(1)
vol	1677.69(17) Å^3
Z	2
density (calcd)	1.256 Mg/m^3
abs coeff	0.241 mm^{-1}
abs cor	empirical (SADABS, 1996, Sheldrick)
T_{min}/T_{max}	0.98/0.98
F(000)	676
crystal size	0.08 × 0.08 × 0.12 mm^3
θ range for data collecn	1.3−26.5°
index ranges	$-13 \le h \le 12$, $-13 \le k \le 13$, $0 \le l \le 20$
no. of rflns collected	8680
no. of indep rflns	6198 (*R*(int) = 0.019)
refinement method	full-matrix least squares on F^2
no. of data/restraints/params	6198/0/370
goodness of fit on F^2	1.393
final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0531, wR2 = 0.1385
R indices (all data)	R1 = 0.0712, wR2 = 0.1520
largest diff peak and hole	0.515 and −0.410 e/Å^3

for P(1)−F(3AA) and 4.071 Å for P(2)−O(1AA). The markedly nonplanar geometry at P(1) (Σ(angles) = 301.2°) indicates that the positive charge in **5c** is localized on P(2) and that the phosphonium−phosphine resonance structure **B** is a more accurate description of the bonding in **5c** than is structure **A**. The transfer



(A)



(B)

of positive charge from the phosphenium to the donor molecule in **5c** is analogous to the charge distribution observed for **I**, where the two planar DBU nitrogens (Σ(angles) = 359.2, 359.9°) are diagnostic for the delocalization of the positive charge.

The P−P bond length of 2.3065(9) Å in **5c** is significantly longer than those in previously reported structurally characterized intramolecular phosphinophosphenium compounds {P[*μ*-N(Me)C(O)N(Me)]$_2$P(NEt$_2$)}(OTf) (2.191 Å),[20] [MePN(Me)C(O)N(Me)P(NEt$_2$)(Ph)](Cl) (2.191 Å),[22] [(Cl$_2$HC)PN(Me)C(O)N(Me)P(CMe$_3$)(Ph)](BPh$_4$) (2.223 Å),[23] [PhPN(H)C(CMe$_3$)=C(H)PPh$_2$](Cl) (2.208 Å),[25] and the zwitterion P[*μ*-N(SiMe$_3$)]P[N(SiMe$_3$)$_2$]N(SiMe$_3$)N(SiMe$_3$)AlCl$_2$N(SiMe$_3$) (2.1051 Å),[26] although this may be due to the fact that there is no chelation of phosphine to phosphenium moieties in **5c**. More surprising, however, is that the P−P bond length in **5c** is also considerably longer than the 2.138(7) and 2.156(10) Å lengths reported for **IV** (crystals of **IV** were disordered such that several atoms each occupy multiple positions in the unit cell), confirming the sterically congested coordination environment of the phosphenium phosphorus center.

The long P(1)−N bonds (1.662(2) and 1.697(2) Å) are also consistent with resonance structure **B**, while the nearly planar N atoms (sum of angles: around N(1), 359.9°; around N(2), 357.5°) presumably reflect the steric demands of the bulky aryl substituents (cf. also the 53 and 76° dihedral angles between the Ar rings and the N−P(1)−N plane). Similar features were observed for the bis(*N*-methylamino)phosphenium cation adduct of the 18e$^-$ [Cp*Fe(CO)$_2$]$^-$ anion (P−N(av) = 1.701(6) Å).[77]

Cationic Rh−Phosphenium Compounds. With a selection of phosphenium cations in hand, we were

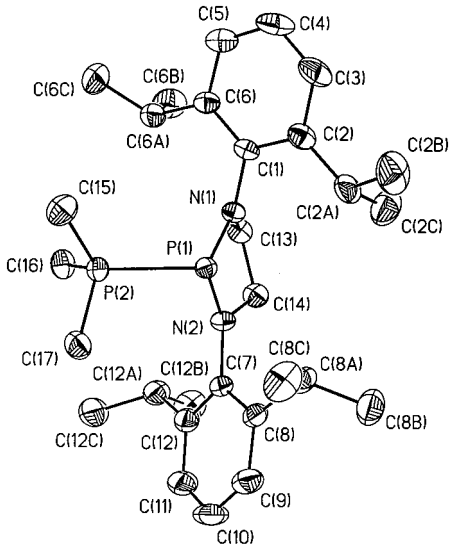


Figure 5. Molecular structure of (PMe$_3$){PN[2,6-(CHMe$_2$)$_2$-C$_6$H$_3$]CH$_2$CH$_2$N[2,6-(CHMe$_2$)$_2$-C$_6$H$_3$]}(OTF) (**5c**). Hydrogens and triflate counterion are omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for ([PMe$_3$]{PN[2,6-(CHMe$_2$)$_2$-C$_6$H$_3$]CH$_2$CH$_2$N-[2,6(CHMe$_2$)$_2$-C$_6$H$_3$]})(OTf) (5c)

P(1)−N(1)	1.661(2)	P(2)−C(16)	1.799(3)
P(1)−N(2)	1.696(2)	N(1)−C(1)	1.449(3)
P(1)−P(2)	2.3065(9)	N(1)−C(13)	1.474(3)
P(2)−C(15)	1.794(3)	N(2)−C(7)	1.440(3)
P(2)−C(17)	1.798(3)	N(2)−C(14)	1.473(3)
N(1)−P(1)−N(2)	92.29(10)	C(16)−P(2)−P(1)	122.96(10)
N(1)−P(1)−P(2)	109.13(8)	C(1)−N(1)−C(13)	121.89(19)
N(2)−P(1)−P(2)	99.74(8)	C(1)−N(1)−P(1)	124.74(17)
C(15)−P(2)−C(17)	106.12(15)	C(13)−N(1)−P(1)	113.30(15)
C(15)−P(2)−C(16)	108.20(14)	C(7)−N(2)−C(14)	120.9(2)
C(17)−P(2)−C(16)	108.85(14)	C(7)−N(2)−P(1)	123.57(17)
C(15)−P(2)−P(1)	108.91(11)	C(14)−N(2)−P(1)	113.06(15)
C(17)−P(2)−P(1)	100.51(10)		

(77) Hutchins, L. D.; Duesler, E. N.; Paine, R. T. *Organometallics* **1982**, *1*, 1254.

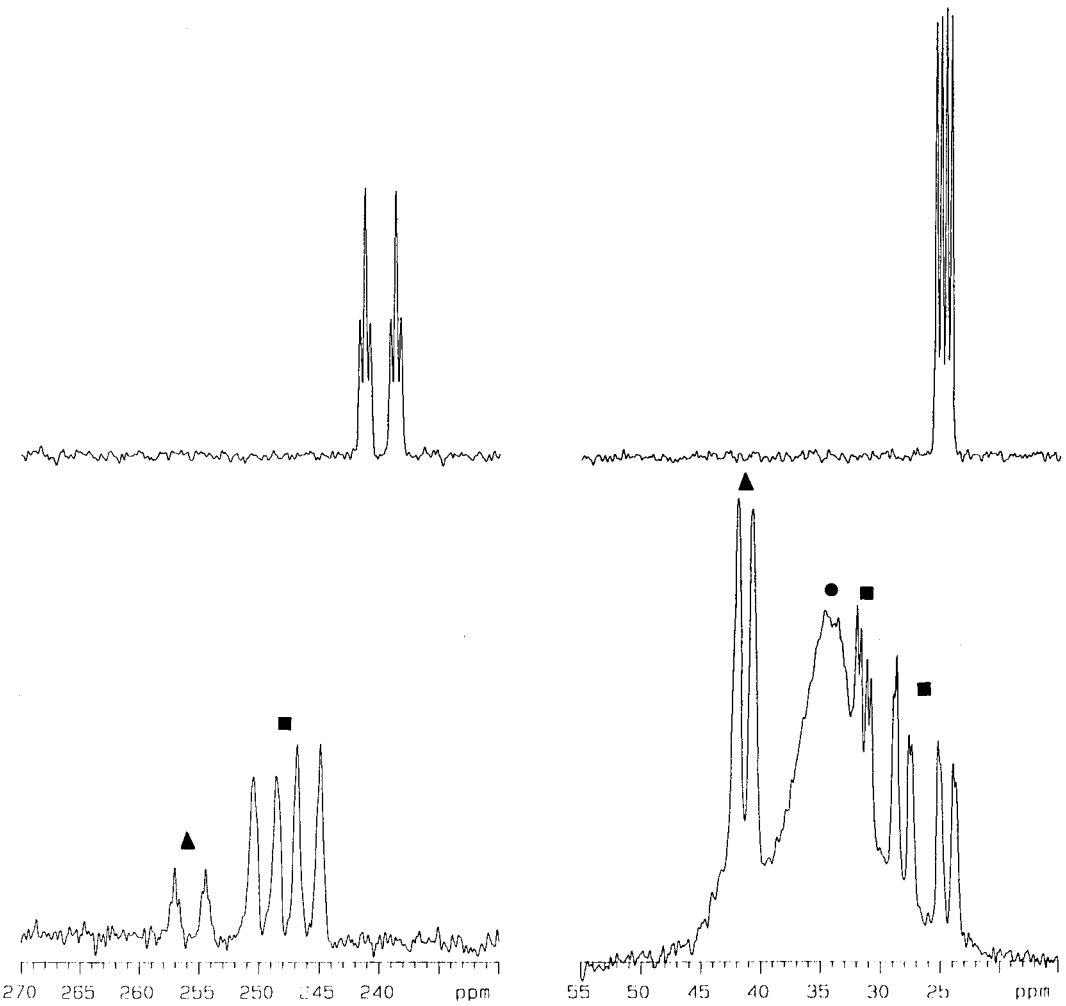


Figure 6. 121 MHz ^{31}P NMR spectra ($CDCl_3$) of (a, top) {*trans*-RhCl(PPh_3)$_2$[PN(4-MeO-C_6H_4)CH_2CH_2N(4-MeO-C_6H_4)]}(OTf) (**6**) and (b, bottom) **4b**/RhCl(PPh_3)$_3$ reaction products. Legend: (●) [Rh(PPh_3)$_3$](OTf); (▲) {*trans*-RhCl(PPh_3)$_2$[PN(2,4,6-Me_3-C_6H_2)CH_2CH_2N(2,4,6-Me_3-C_6H_2)]}(OTf) (**7b**); (■) {*cis*-RhCl(PPh_3)$_2$[PN(2,4,6-Me_3-C_6H_2)CH_2CH_2N(2,4,6-Me_3-C_6H_2)]}(OTf) (**7a**).

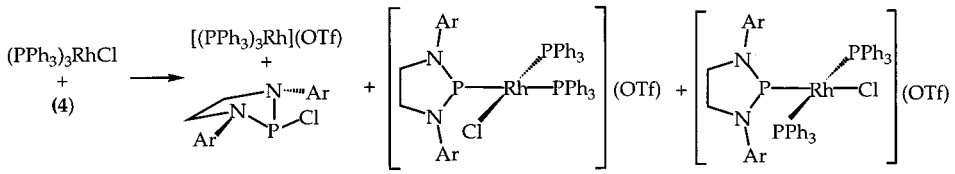
interested to see whether well-defined metallophosphenium cations could be obtained from the direct addition of **4** to neutral transition-metal-containing species. Despite an early report by Montemayor et al.[44] that the cationic iron−phosphenium complex {Fe[PN(Me)CH_2-CH_2N(Me)](CO)$_4$}(PF_6) could be obtained from addition of [PN(Me)CH_2CH_2N(Me)](PF_6) to Fe(CO)$_5$ or Fe$_2$(CO)$_9$, this synthetic approach has found use only in a single report of the in situ generation of Rh−phosphenium-based hydroformylation catalysts.[65] For our investigations, we chose to utilize phosphine-containing compounds of rhodium for initial study, in part on the basis of the profusion of Rh−phosphine compounds used for homogeneous catalysis[78] and on the potential for facile product identification by ^{31}P NMR spectroscopy.[79]

Addition of 1 equiv of the methoxy-substituted **4a** to a $CDCl_3$ solution of Wilkinson's catalyst, RhCl(PPh_3)$_3$, results in the immediate formation of a clear, bright yellow solution. ^{1}H NMR spectroscopy revealed the complete consumption of starting **4a** and formation of a single new heterocycle-containing complex, **6**, as evidenced by the single set of resonances at δ 3.75 (d, J = 7.1 Hz, 4H, NCH_2) and 3.86 (s, 6H, OCH_3). The presence of overlapping multiplets for the various aryl protons complicated further identification by ^{1}H NMR.

^{31}P NMR, however, proved invaluable in determining the course of this reaction, confirming that both **4a** and the Rh starting material had been consumed. A singlet for free PPh_3 and an AX_2 spin system consisting of an upfield doublet of doublets (24.91 ppm, $^1J_{Rh-P}$ = 102, $^2J_{P-P}$ = 51 Hz) and a downfield doublet of triplets (240.18 ppm, $^1J_{Rh-P}$ = 311, $^2J_{P-P}$ = 51 Hz) (Figure 6a), in a 1:2:1 ratio, were the only signals observed in the crude reaction mixture. The coupling of the phosphenium resonance to two equivalent phosphines indicates that the phosphine *trans* to the halide in RhCl(PPh_3)$_3$ has been replaced by the phosphenium ligand. The large downfield shift (∼100 ppm relative to **4a**) of the deshielded phosphenium resonance argues strongly against formation of the isomeric Rh−chlorophosphine complex

(78) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis: the Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes*; Wiley: New York, 1992.
(79) Pregosin, P. S.; Kunz, W. R. *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*; Springer-Verlag: New York, 1979.

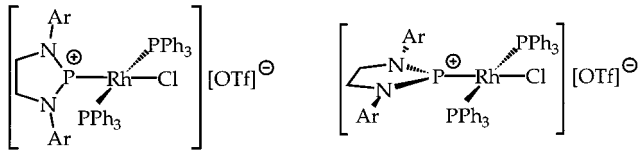
Scheme 3



Ar = 2,6-*i*Pr$_2$-Ph **(4c)**	100 %	0 %	0 %
Ar = 2,4,6-Me$_3$-Ph **(4b)**	53 %	41 %	6 %
Ar = 4-MeO-Ph **(4a)**	0 %	0 %	100 %

{Rh(PPh$_3$)$_2$[P(Cl)N(4-MeO-C$_6$H$_4$)CH$_2$CH$_2$N(4-MeO-C$_6$H$_4$)]}(OTf). The large $^1J_{Rh-P}$ of the downfield resonance is also consistent with a phosphenium ligand residing *trans* to a halide (rather than to a phosphine).[79] Preparative-scale reactions (CH_2Cl_2) afford **6** as an orange, toluene-insoluble powder in 80% yield; ^{13}C NMR spectroscopy and elemental analysis, as well as the fully resolved ^{1}H NMR spectra (see Experimental Section) all support the assignment of **6** as {*trans*-RhCl(PPh$_3$)$_2$[PN(4-MeO-C$_6$H$_4$)CH$_2$CH$_2$N(4-MeO-C$_6$H$_4$)]}(OTf).

In the absence of a crystal structure, it is difficult to unambiguously establish details of the bonding within the cation of **6**, particularly to distinguish between Rh(I)−phosphenium structures **C** and **D**, or to determine the extent of M−P multiple bonding. In **C** and **D**,



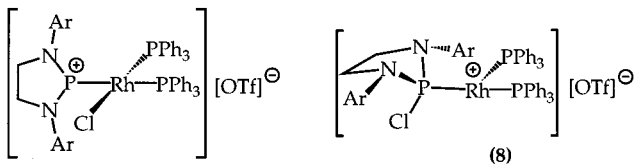
(C) **(D)**

the positively charged phosphenium ion acts as a two-electron σ-donor to the Rh center, with the vacant π-symmetry orbital on the phosphenium ion (localized on phosphorus) available for back-bonding from Rh. Steric interactions between the phosphenium Ar substituents and the PPh$_3$ ligands are minimized in structure **C** through rotation of the phosphenium heterocycle out of the Cl−Rh−*P*Ph$_3$ plane; this orientation also provides favorable overlap of the vacant phosphenium π-symmetry orbital with a filled d orbital on Rh. For these reasons we favor structure **C** as the most accurate representation of the bonding in **6**.[80] Although suggestive of M−P multiple bonding character, the large (311 Hz) $^1J_{Rh-P}$ value in **6** may result from factors other than π-donation from the Rh center; a similar $^1J_{Rh-P}$ value (300 Hz) is observed for the neutral Rh−chlorophosphine complex *trans*-RhCl(PPh$_3$)$_2$[P(Cl)N(4-MeO-C$_6$H$_4$)CH$_2$CH$_2$N(4-MeO-C$_6$H$_4$)].[81]

The steric demands imparted by the phosphenium aryl substituents dramatically influence the ability of **4** to form stable metallophosphenium compounds (Scheme 3). In contrast to that observed for **4a**, addition of 1 equiv of the isopropyl-substituted **4c** to a $CDCl_3$ solution of Wilkinson's catalyst results in quantitative formation of [Rh(PPh$_3$)$_3$](OTf) and chlorophosphine **3c**, with no metallophosphenium species observed at any time in the crude reaction mixture (^{31}P NMR).

The analogous reaction using mesityl-substituted **4b** affords a mixture of products; ^{31}P NMR spectroscopy on the crude reaction mixture shows the complete consumption of all starting materials and exhibits resonances attributable to [Rh(PPh$_3$)$_3$](OTf)/**3b** (53%), free PPh$_3$, and *two* metallophosphenium compounds, **7a** and **7b** (Figure 6b). The minor metallophosphenium complex (6%, **7b**) exhibits a ^{31}P spectrum with an AX$_2$ splitting pattern similar to that of **6**: an upfield doublet of doublets (31.38 ppm, $^1J_{Rh-P}$ = 106 Hz, $^2J_{P-P}$ = 43 Hz), and a downfield doublet of triplets (255.76 ppm) with a large $^1J_{Rh-P}$ value (316 Hz) and a small $^2J_{P-P}$ value (not completely resolved). Accordingly, **7b** is assigned as {*trans*-RhCl(PPh$_3$)$_2$[PN(2,4,6-Me$_3$-C$_6$H$_2$)CH$_2$CH$_2$N(2,4,6-Me$_3$-C$_6$H$_2$)]}(OTf).

The major phosphenium-containing product (41%, **7a**) exhibits an AXY splitting pattern, with two upfield and one downfield resonances. The upfield resonances consist of a doublet of doublets of doublets ($^2J_{P-P}$ = 451 Hz, $^1J_{Rh-P}$ = 158 Hz, $^2J_{P-P}$ = 21 Hz) at 26.39 ppm, and an apparent doublet of doublets ($^1J_{Rh-P}$ = 153 Hz, smaller additional coupling not resolved) at 41.32 ppm; the downfield signal (247.63 ppm) is a doublet of doublet of doublets ($^2J_{P-P}$ = 448 Hz, $^1J_{Rh-P}$ = 234 Hz, plus an additional, unresolved, smaller coupling). Both the large $^2J_{P-P}$ value and the small $^1J_{Rh-P}$ value of **7a** (relative to **6** and **7b**) are indicative of a *trans* phosphenium−phosphine arrangement. The downfield chemical shift of the most deshielded resonance argues against the T-shaped Rh cation **8** or the corresponding square



(7a) **(8)**

planar complex with a bound triflate. Accordingly, we assign **7a** as the square-planar Rh(I) complex {*cis*-RhCl(PPh$_3$)$_2$[PN(2,4,6-Me$_3$-C$_6$H$_2$)CH$_2$CH$_2$N(2,4,6-Me$_3$-C$_6$H$_2$)]}-

(80) This phosphenium orientation is also supported by DFT calculations: Abrams, M. B.; Martin, R. L.; John, K. D.; Baker, R. T. Manuscript in preparation.

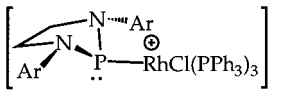
(81) Abrams, M. B.; Baker, R. T. Unpublished results.

(OTf) with the sterically more demanding mesityl substituents enforcing a *cis* disposition of triphenylphosphine ligands.

Conclusions

The bis(arylamino)phosphenium cations **4a**−**e** reported herein have been shown to provide steric tunability in the stability of their phosphine adducts and in their variety of reactions with Wilkinson's catalyst. The chlorophosphines **3a**−**c** also exhibit hindered N−C_{Ar} bond rotation for bulky N−Ar substituents. The structural information provided by the first well-behaved, single-crystal X-ray diffraction study on an intermolecular phosphinophosphenium adduct reveals additional steric consequences, both in the long P−P bond distance and in the structure and bonding within the phosphenium ligand array.

The Rh complexes **6** and **7a**,**b** are the first well-characterized, cationic group 9 complexes incorporating phosphenium ligands. Of particular interest is the bonding within **6** and **7**. All available spectroscopic evidence (^{31}P chemical shifts and Rh−P and P−P coupling constants, in particular) indicate that these compounds contain square-planar, cationic, Rh(I) fragments (with the phosphenium ligand acting as a two-electron σ-donor), as opposed to Rh(III)−phosphido species such as **E**. This is in contrast to the spectroscopically and crystallographically characterized phosphine adducts **5**, which are best described as phosphinophosphonium compounds, where the positive charge from the phosphenium ion has been transferred to the coordinated PMe_3 ligand (structure **B**).



(E)

This behavior has been noted previously by Paine et al. in comparing phosphenium complexes of the 16e$^-$ $[CpMo(CO)_2]^-$ and 18e$^-$ $[CpFe(CO)_2]^-$ anions.[31,77] The short M−P bond and planar phosphorus center in the former are consistent with both donor and acceptor functions for the phosphenium ligand, while the long Fe−P and P−N bonds and pyramidal phosphorus in the latter are more in concert with an iron phosphido complex with a stereochemically active lone pair at phosphorus. While the bonding in Rh complexes **7a**,**b** is also likely to involve both donor and acceptor functions for the phosphenium ligand, it is difficult to predict a priori how this balance will be affected by changing from a *trans* chloride in **7b** to a *trans* phosphine in **7a**. We are currently applying density functional theory to address these questions and others that have arisen from analogous coordinatively unsaturated group 10 complexes we have recently prepared.[81] Further investigations also include the use of electron-withdrawing N-aryl substituents to assess the effects of P−N π-bonding in precious-metal phosphenium complexes.

Experimental Section

All reactions were conducted under nitrogen using standard Schlenk, cannula, and glovebox techniques. Toluene, diethyl ether, and THF were purified using the system described by Pangborn et al.[82] Triethylamine was purchased from Fluka, dried over CaH_2, and vacuum-distilled prior to use. Chloroform was dried over P_2O_5 and vacuum-distilled prior to use. $CDCl_3$ (Acros) was dried over P_2O_5, vacuum-distilled, and stored over 4 Å molecular sieves. CD_2Cl_2 (Acros) and toluene-d_8 (Aldrich) were stored over 4 Å sieves. Deuteriobenzene (Acros) was distilled from Na or dried over sieves prior to use. Methanol, ethanol, 2,6-diisopropylaniline (Fluka), glyoxal, *p*-anisidine, 2,4,6-trimethylaniline, sodium borohydride, silver triflate, and trimethylphosphine (Aldrich) were used as received. Phosphorus trichloride (Acros) was transferred to a Schlenk flask and stored under N_2. $TlB[3,5\text{-}(CF_3)_2\text{-}C_6H_3]_4$[83] and $RhCl(PPh_3)_3$[84,85] were prepared according to literature procedures. NMR spectra were recorded on a Varian Unity Inova 300 spectrometer (299.93 MHz for ^{1}H, 75.42 MHz for ^{13}C, 121.42 MHz for ^{31}P). Temperatures were calibrated using external methanol or ethylene glycol standards. Elemental analysis was performed using a Perkin-Elmer 2400 Series II CHNS/O analyzer. Although hydrogen and nitrogen analyses were satisfactory, carbon analysis often provided values slightly below the expected numbers; abnormally low carbon values, in addition to being internally consistent from run to run and from sample to sample, were observed for nearly all of the compounds analyzed.

(4-MeO-C_6H_4)N=CHCH=N(4-MeO-C_6H_4) (1a). Anisidine (48.90 g. 397 mmol, 2.00 equiv) and EtOH (750 mL) were placed in a 1 L pear-shaped flask equipped with a magnetic stir bar. Glyoxal (28.79 g, 40 wt % in H_2O, 198 mmol, 1.00 equiv) was pipetted into the blackish solution, and the contents of the flask were stirred at room temperature for 18 h; a bright yellow solid began precipitating from the solution within minutes of the glyoxal addition. The solution was filtered using a medium-porosity filter frit, yielding a large amount of flocculent yellow EtOH/H_2O-insoluble solid. The solid was washed once with 60 mL of toluene (0 °C), and was dried in vacuo, yielding 35.67 g of yellow solid. A second crop was obtained by concentrating the EtOH/H_2O solution to a volume of ∼40 mL on a rotavap (50 °C) and then cooling (0 °C) and filtering the solution; the solid was then washed with 30 mL of 0 °C EtOH and 60 mL of 0 °C toluene, yielding an additional 1.01 g of diimine after drying in vacuo. Total isolated yield: 36.68 g (137 mmol, 69% yield). ^{1}H NMR (δ, in $CDCl_3$): 3.85 (s, 6H, OCH_3), 6.95 (d, J = 9.0 Hz, 4H, C_6H_4), 7.34 (d, J = 8.8 Hz, 4H, C_6H_4), 8.42 (s, 2H, NC*H*).

(2,4,6-Me_3-C_6H_2)N=CHCH=N(2,4,6-Me_3-C_6H_2) (1b). To a 500 mL round-bottom flask equipped with a magnetic stir bar was added 250 mL of ethanol and 15.115 g (111.8 mmol, 2.00 equiv) of 2,4,6-Me_3PhNH_2. Glyoxal (8.106 g, 40 wt % solution, 55.86 mmol, 1.00 equiv) was added to the clear, faint yellow solution, and the resulting bright yellow solution was stirred at room temperature for 14 h. The solution was filtered, affording 8.035 g of a bright yellow EtOH/H_2O-insoluble solid (after drying in vacuo). A second crop of 1.809 g of yellow needles precipitated from the EtOH/H_2O solution upon standing over the course of 3 weeks; additional crops of 1.487 and 2.335 g (after washing with small aliquots of 0 °C ethanol and drying in vacuo) of yellow solid were obtained by concentrating the EtOH/H_2O solution on a rotavap (50 °C), cooling to 0 °C, and isolating the resultant bright yellow solids by filtration. Total isolated yield: 13.666 g, 46.7 mmol, 84%. ^{1}H NMR (δ, in $CDCl_3$): 2.20 (s, 12 H, 2,6-(CH_3)$_2$-C_6H_2), 2.33 (s, 6H, 4-CH_3-C_6H_2), 6.95 (s, 4H, C_6H_2), 8.15 (s, 2H, NC*H*).

[2,6-($CHMe_2$)$_2$-C_6H_3]N=CHCH=N[2,6-($CHMe_2$)$_2$-C_6H_3] (1c). A 250 mL round-bottom flask equipped with a magnetic stir

(82) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.
(83) Hughes, R. P.; Lindner, D. C.; Rheingold, A. L.; Yap, G. P. A. *Inorg. Chem.* **1997**, *36*, 1726.
(84) Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G. *J. Chem. Soc. A* **1966**, 1711.
(85) Osborn, J. A.; Wilkinson, G. *Inorg. Synth.* **1967**, *10*, 67.

bar was charged with 10.043 g (56.65 mmol, 1.99 equiv) of 2,6-diisopropylaniline and 130 mL of ethanol. Glyoxal (4.173 g, 40 wt % in H_2O, 28.45 mmol, 1.00 equiv) was added dropwise to the stirred solution, which acquired a bright yellow color within minutes of the glyoxal addition; the solution was refluxed for 12 h and then cooled to room temperature. The volume of solvent was reduced to ~100 mL on a rotavap (45 °C), and the yellow insoluble material was isolated by filtration and was then washed with cold ethanol. A second crop was obtained by further concentration of the mother liquor, filtration, and washing of the resultant solid with two 5 mL portions of 0 °C ethanol. The combined yellow solids were crushed with a mortar and pestle, washed twice with 20 mL aliquots of 0 °C ethanol, and dried in vacuo. Isolated yield: 8.313 g of yellow powder, 22.10 mmol, 78% yield. ^{1}H NMR (δ, in $CDCl_3$, 25 °C): 1.24 (d, J = 6.8 Hz, 24H, $CH(CH_3)_2$), 2.97 (septet, J = 6.8 Hz, 4H, $CH(CH_3)_2$), 7.21 (m, 6H, overlapping C_6H_3), 8.13 (s, 2H, NC*H*).

(4-MeO-C_6H_4)N(H)CH_2CH_2N(H)(4-MeO-C_6H_4) (2a). A 3 L three-necked round-bottom flask, equipped with a stir bar, a solid addition funnel, a solution addition funnel, and a reflux condenser, was charged with 36.62 g (136.5 mmol, 1.0 equiv) of **1a** and 1750 mL of EtOH. Sodium borohydride (51.61 g, 1364 mmol, 9.99 equiv) was added to the solution (via the addition funnel) over the course of 135 min. The solution was then heated with a heating mantle and was refluxed for 60 min. The colorless solution and white precipitate were cooled to room temperature and were stirred at room temperature overnight. A saturated NaCl (H_2O) solution (350 mL) was added to the solution via the solution addition funnel; the rate of addition was adjusted to maintain a steady reflux. After the solution was cooled to room temperature, the white solid was removed from the light orange solution by filtration using a medium porosity filter frit; the EtOH/H_2O insolubles were washed with 1500 mL of H_2O and were dried in vacuo. The white solid was then dissolved in THF (450 mL), and stirred overnight over 4 Å molecular sieves; after filtration though a medium-porosity filter frit, solvent was removed from the colorless solution in vacuo, affording 26.2 g of white solid. An additional 6.17 g of diamine (after drying over sieves in THF) was obtained as a tan microcrystalline solid by extraction of the combined EtOH/aqueous solutions with $CHCl_3$; total isolated yield of (4-CH_3O-C_6H_4)N(H)CH_2CH_2N(H)(4-CH_3O-C_6H_4) 32.4 g (118.9 mmol, 87% yield). ^{1}H NMR (δ, in $CDCl_3$): 3.34 (s, 4H, NCH_2), 3.68 (s, 2H, N*H*), 3.77 (s, 6H, OCH_3), 6.63 (d, J = 8.8 Hz, 4H, C_6H_4), 6.82 (d, J = 9.0 Hz, 4H, C_6H_4).

(2,4,6-Me_3-C_6H_2)N(H)CH_2CH_2N(H)(2,4,6-Me_3-C_6H_2) (2b). A 250 mL round-bottom flask, equipped with a magnetic stir bar, a solid addition funnel, and a water-cooled reflux condenser, was charged with 2.455 g (8.39 mmol, 1.00 equiv) of **1b**. Ethanol (125 mL) was added to the flask, and the bright yellow solution cooled to 0 °C. Sodium borohydride (3.178 g, 84.0 mmol, 10.00 equiv) was added to the solution via the addition funnel over the course of 55 min. The 0 °C bath was removed and replaced with a heating mantle; the solution was refluxed for 45 min, affording a colorless solution and a white precipitate. The solution was cooled to 25 °C, and 20 mL of an aqueous saturated NaCl solution was added slowly to the flask, acquiring and then maintaining a gentle reflux. Upon cooling to room temperature, the solution was filtered using a medium-porosity filter frit, and the white insoluble material was washed once with 50 mL of H_2O. The combined ethanol and aqueous solutions were diluted with 40 mL of additional water and extracted with 60 mL of chloroform. The organic layer was separated, and volatiles were removed on a rotavap, yielding a small amount of yellow oil which crystallized upon standing in air. The yellow solid was then dissolved in 40 mL of THF and stirred over 4 Å sieves for 2 days. The solution was filtered, and volatiles were removed in vacuo, leaving a clear yellow oil which crystallized upon standing under N_2, affording 1.905 g of a yellow microcrystalline solid (6.42 mmol, 77% yield). ^{1}H NMR (δ, in $CDCl_3$): 2.28 (s, 6H, 4-CH_3-C_6H_2), 2.33 (s, 12H, 2,6-$(CH_3)_2$-C_6H_2), 3.19 (s, 4H, NCH_2), 3.32 (s, 2H, N*H*), 6.87 (s, 4H, C_6H_2). ^{13}C{^{1}H} NMR (δ, in $CDCl_3$): 18.3 (4-CH_3-C_6H_2), 20.5 (2,6-$(CH_3)_2$-C_6H_2), 49.3 (NCH_2), 129.5 (C_6H_2), 129.8 (C_6H_2), 131.4 (C_6H_2), 143.3 (C_6H_2).

[2,6-$(CHMe_2)_2$-C_6H_3]N(H)CH_2CH_2N(H)[2,6-$(CHMe_2)_2$-C_6H_3] (2c). A 200 mL round-bottom flask, equipped with a magnetic stir bar, was charged with 3.141 g (8.341 mmol, 1.00 equiv) of **1c** and 125 mL of ethanol. The solution was cooled to 0 °C, and 3.220 g (85.10 mmol, 10.2 equiv) of sodium borohydride was added in small batches over the course of 20 min. The bright yellow solution with white precipitate was stirred at 0 °C for 10 min and then refluxed for 105 min. The solution was cooled to 50 °C, and 20 mL of a saturated NaCl/H_2O solution was added slowly to the pale orange solution and white precipitate, maintaining a gentle reflux. After it was stirred at room temperature for an additional 30 min, the solution was diluted with 100 mL of water and 75 mL of chloroform. The organic layer was separated and washed with 10 mL of water. Volatiles were removed on a rotavap from the organic layer, and the resulting pale orange solid was dried in vacuo, dissolved in 100 mL of THF, and dried over 4 Å sieves. After filtering and removal of volatiles, 2.628 g of a pale orange solid was isolated (6.90 mmol, 83% yield). ^{1}H NMR (δ, in $CDCl_3$): 1.23 (d, J = 6.8 Hz, 24H, $CH(CH_3)_2$), 3.14 (s, 4H, NCH_2), 3.32 (s, 2H, N*H*), 3.34 (septet, J = 6.8 Hz, 4H, $CH(CH_3)_2$), 7.09 (overlapping multiplets, 6H, C_6H_3). ^{13}C{^{1}H} NMR (δ, in $CDCl_3$): 24.24 ($CH(CH_3)_2$), 27.78 ($CH(CH_3)_2$), 52.34 (NCH_2), 123.59 (C_6H_3), 123.84 (C_6H_3), 142.50 (C_6H_3), 143.34 (C_6H_3).

ClP[N(4MeO-C_6H_4)CH_2CH_2N(4-MeO-C_6H_4) (3a). A 100 mL Schlenk flask, equipped with a magnetic stir bar, was charged with 801 mg (2.94 mmol, 1.02 equiv) of **2a**, 45 mL of CH_2Cl_2, and 7 mL (50 mmol, 17 equiv) of Et_3N; the resulting clear, colorless solution was cooled to 0 °C. Phosphorus trichloride (0.25 mL, 2.87 mmol, 1.00 equiv) was syringed dropwise into the cooled solution against a N_2 counterflow, accompanied by the precipitation of a white solid. The solution was stirred at 0 °C for 30 min, was warmed to 25 °C, and was stirred at room temperature for an additional 90 min. Volatiles were removed from the light yellow solution, and the solids were dried in vacuo. The resulting light yellow solid was washed once with 20 mL and once with 10 mL of THF, and Et_3NHCl was removed by filtration using a medium-porosity filter frit. Solvent was removed from the combined organics, leaving a pale yellow solid (864 mg, 2.57 mmol, 89% yield). Anal. Calcd for $C_{16}H_{18}N_2O_2PCl$: C, 57.06; H, 5.40; N, 8.32. Found: C, 55.59, 56.30, 56.24; H, 5.69, 5.73, 5.88; N, 8.02, 8.15, 8.08. ^{31}P{^{1}H} NMR (δ, in $CDCl_3$): 138.7. ^{1}H NMR (δ, in $CDCl_3$): 3.81 (s, 6H, OCH_3), 3.92 (br, 4H, NCH_2), 6.91 (m, J = 7.6 Hz, 2H, C_6H_4), 7.13 (m, J = 6.8 Hz, 2H, C_6H_4). ^{13}C{^{1}H} NMR (δ, in $CDCl_3$): 48.9 (d, J_{P-C} = 10 Hz, NCH_2), 55.6 (s, OCH_3), 115.0 (s, C_6H_4), 119.0 (d, J_{P-C} = 13 Hz, C_6H_4), 135.8 (d, J_{P-C} = 14 Hz, C_6H_4), 155.5 (s, C_6H_4).

ClP[N(2,4,6-Me_3-C_6H_2)CH_2CH_2N(2,4,6-Me_3-C_6H_2) (3b). A 100 mL Schlenk flask was charged with 1.872 g (6.31 mmol, 1.00 equiv) of **2b**, 45 mL of CH_2Cl_2, and 16 mL (114.7 mmol, 18.2 equiv) of Et_3N, and the clear, pale yellow solution was cooled to 0 °C. PCl_3 (0.55 mL, 6.30 mmol, 1.00 equiv) was syringed dropwise into the cooled solution, and the resulting light yellow solution with fine white precipitate was stirred at 0 °C for 30 min. The 0 °C bath was removed, and the solution was stirred for an additional 95 min at room temperature. Volatiles were removed, and the remaining light yellow solid was dried in vacuo. The solid was washed once with 40 mL of Et_2O and once with 10 mL of Et_2O. The Et_2O-insoluble solid was extracted once with 40 mL of THF; volatiles were removed in vacuo from the THF solution, yielding 1.393 g of white solid. Additional crops of 113 and 97 mg of white solid were obtained from additional THF extractions of the Et_2O-

insoluble solid. Total isolated yield: 1.414 g, 3.92 mmol, 62%. Anal. Calcd for $C_{20}H_{126}N_2PCl$: C, 66.56; H, 7.28; N, 7.76. Found: C, 61.45. 60.67, 60.17; H, 8.11, 8.01, 7.96; N, 7.10, 7.06, 6.93. ^{1}H NMR (δ, in $CDCl_3$, 25 °C): 2.31 (s, 6H, 2,4,6-(CH_3)$_3$-C_6H_2), 2.45 (br, 12H, 2,4,6-(CH_3)$_3$-C_6H_2), 3.54 (br, 2H, NCH_2), 4.13 (br, 2H, NCH_2), 7.03 (s, 4H, C_6H_2).

ClP[2,6-(CHMe$_2$)$_2$-C_6H_3]CH$_2$CH$_2$N[2,6-(CHMe$_2$)$_2$-C_6H_3] (3c). A 200 mL Schlenk flask was charged with 2.016 g (5.59 mmol,1.00 equiv) of **2c**, 100 mL of CH_2Cl_2, and 12 mL (86.0 mmol, 15.4 equiv) of Et_3N, and the solution was cooled to 0 °C. PCl_3 (0.49 mL, 5.62 mmol, 1.01 equiv) was syringed into the cooled solution dropwise against a N_2 counterflow, and the light yellow solution was stirred at 0 °C for 3.5 h. Volatiles were removed, and the resultant light yellow solid was dried in vacuo. Diethyl ether (35 mL) was added to the solid, and a fine white solid was removed by filtration from the clear yellow liquid; the white solid was washed twice with 20 mL portions of Et_2O. Volatiles were removed from the combined organics, yielding 1.836 g of light yellow solid (4.32 mmol, 77% yield). Anal. Calcd for $C_{26}H_{38}N_2PCl$: C, 70.16; H, 8.62; N, 6.30. Found: C, 69.49, 69.55, 69.48; H, 9.07, 9.24, 9.19; N, 7.05, 6.12, 6.18. ^{1}H NMR (δ, in $CDCl_3$): 1.29 (d, J = 7.3 Hz, 6H, CH(CH_3)$_2$), 1.31 (d, J = 7.3 Hz, 6H, CH(CH_3)$_2$), 1.32 (d, J = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.35 (d, J = 6.4 Hz, 6H, CH(CH_3)$_2$), 3.38 (septet, J = 6.6 Hz, 2H, CH(CH$_3$)$_2$), 3.60 (m, 2H, NCH_2), 3.84 (septet, J = 6.8 Hz, 2H, CH(CH$_3$)$_2$), 4.12 (m, 2H, NCH_2), 7.28 (overlapping multiplets, 6H, C_6H_3). ^{13}C{^{1}H} NMR (δ, in $CDCl_3$): 24.36 (d, J_{P-C} = 3 Hz, CH(CH$_3$)$_2$), 24.56 (s, CH(CH$_3$)$_2$), 25.25 (s, CH(CH$_3$)$_2$) 25.42 (s, CH(CH$_3$)$_2$), 28.48 (s, CH(CH$_3$)$_2$), 28.98 (d, J_{P-C} = 6 Hz, CH(CH$_3$)$_2$), 54.76 (d, J_{P-C} = 10 Hz, NCH$_2$), 123.96 (s, C_6H_4), 124.94 (s, C_6H_4), 128.20 (s, C_6H_4), 134.90 (d, J_{P-C} = 13 Hz, C_6H_4), 147.55 (d, J_{P-C} = 3 Hz, C_6H_4), 149.90 (d, J_{P-C} = 4 Hz, C_6H_4).

[PN(4-MeO-C_6H_4)CH$_2$CH$_2$N(4-MeO-C_6H_4)](OTf) (4a). A 250 mL round-bottom flask was wrapped in Al foil and charged with 2.274 g (6.75 mmol, 1.00 equiv) of **3a** and 80 mL of toluene. Silver triflate ($AgOSO_2CF_3$, AgOTf, 1.732 g, 6.74 mmol, 1.00 equiv) was added slowly to the stirred solution, and the solution was stirred at room temperature for 2.5 days. The solution with yellow solid was filtered through a medium-porosity filter frit; volatiles were removed from the bright yellow toluene solution, affording 496 mg of bright yellow powder. Additional crops of 870, 879, and 297 mg of bright yellow powder were obtained by repeated (3−4×) washings of the filter cake with toluene (50 mL aliquots) and removal of volatiles from the combined organics. Total isolated yield: 2.542 g, 5.65 mmol, 84% yield. Anal. Calcd for $C_{17}H_{18}N_2O_5PSF_3$: C, 45.33; H, 4.04; N, 6.22. Found: C, 45.46, 45.48, 45.38; H, 4.54, 4.57, 4.46; N, 6.05, 5.92, 6.01. ^{1}H NMR (δ, in $CDCl_3$): 3.82 (s, 6H, OCH_3), 4.21 (d, J = 5.4 Hz, 4H, NCH_2), 6.94 (m, J = 9.0 Hz, 2H, C_6H_4), 7.30 (m, J = 7.3 Hz, 2H, C_6H_4). ^{13}C-{^{1}H} NMR (δ, in $CDCl_3$): 52.2 (d, J_{P-C} = 9 Hz, NCH$_2$), 55.6 (s, OCH$_3$), 115.1 (s, C_6H_4), 119.7 (quartet, J_{C-F} = 319 Hz, OSO_2CF_3), 121.7 (d, J_{P-C} = 10 Hz, C_6H_4), 132.2 (d, J_{P-C} = 16 Hz, C_6H_4), 158.0 (s, C_6H_4).

[PN(2,4,6-Me$_3$-C_6H_2)CH$_2$CH$_2$N(2,4,6-Me$_3$-C_6H_2)](OTf) (4b). A 200 mL round-bottom flask was charged with 1.334 g (3.70 mmol, 1.00 equiv) of **3b** and 50 mL of toluene, giving a colorless solution with a suspension of white solid. The flask was wrapped in Al foil, and AgOTf (949 mg, 3.69 mmol, 1.00 equiv) was slowly added to the stirred solution; the solution was stirred at room temperature for 2 h and was then filtered through a medium-porosity frit, affording a small amount of white solid and a clear, colorless solution. Volatiles were removed from the toluene solution, yielding 1.588 g (3.35 mmol, 91% yield) of white solid. Anal. Calcd for $C_{21}H_{26}N_2O_3PSF_3$: C, 53.15; H, 5.53; N, 5.90. Found: C, 52.72, 52.81, 52.13; H, 6.00, 6.56, 5.91; N, 5.82, 5.82, 5.68. ^{1}H NMR (δ, in $CDCl_3$): 2.31 (s, 6H, 2,4,6-(CH_3)$_3$-C_6H_2), 2.43 (s, 12H, 2,4,6-(CH_3)$_3$-C_6H_2), 3.99 (d, J = 5.1 Hz, 4H, NCH_2), 6.98 (s, 4H, C_6H_2). ^{13}C{^{1}H} NMR (δ, in $CDCl_3$): 18.47 (d, J_{P-C} = 2 Hz, (CH$_3$)$_3$-C_6H_2), 20.83 (s, (CH$_3$)$_3$-C_6H_2), 53.54 (d, J_{P-C} = 9 Hz, NCH$_2$), 119.37 (quartet, J_{C-F} = 319 Hz, OSO_2CF_3), 129.97 (s, C_6H_2), 132.35 (d, J_{P-C} = 12 Hz, C_6H_2), 136.10 (d, J_{P-C} = 4 Hz, C_6H_2), 138.49 (s, C_6H_2).

{PN[2,6-(CHMe$_2$)$_2$-C_6H_3]CH$_2$CH$_2$N[2,6-(CHMe$_2$)$_2$-C_6H_3]}-(OTf) (4c). A 100 mL round-bottom flask was wrapped in Al foil and charged with 1.0043 g (2.36 mmol, 1.01 equiv) of **3c** and 45 mL of toluene. AgOTf (601 mg, 2.34 mmol, 1.00 equiv) was added slowly to the stirred solution, and the resulting solution was stirred at 25 °C for 4 h. The solution was filtered through a medium-porosity filter frit, and volatiles were removed from the clear, light yellow toluene solution, yielding 1.161 g of white solid after drying in vacuo (2.08 mmol, 89% yield). Anal. Calcd for $C_{27}H_{38}N_2O_3PSF_3$: C, 58.04; H, 6.87; N, 5.02. Found: C, 57.09, 57.67, 56.67; H, 7.34, 7.35, 7.21; N, 4.85, 5.33, 4.79. ^{1}H NMR (δ, in $CDCl_3$): 1.30 (d, J = 6.8 Hz, 12H, CH(CH_3)$_2$), 1.35 (d, J = 6.8 Hz, 12H, CH(CH_3)$_2$), 3.34 (septet, J = 6.8 Hz, 4H, CH(CH$_3$)$_2$), 3.99 (d, J = 5.9 Hz, 4H, NCH_2), 7.25 (m, 4H, C_6H_3), 7.37 (m, 4H, C_6H_3). ^{13}C{^{1}H} NMR (δ, in $CDCl_3$): 24.35 (s, CH(CH$_3$)$_2$), 25.53 (s, CH(CH$_3$)$_2$), 28.99 (s, CH-(CH$_3$)$_2$), 56.04 (d, J_{P-C} = 10.6 Hz, NCH$_2$), 119.20 (quartet, J_{C-F} = 320 Hz, OSO_2CF_3), 124.76 (s, C_6H_3), 129.35 (s, C_6H_3), 132.46 (d, J_{P-C} = 12.1 Hz, C_6H_3), 147.35 (d, J_{P-C} = 3.5 Hz, C_6H_3).

[PN(4-CH$_3$O-C_6H_4)CH$_2$CH$_2$N(4-CH$_3$O-C_6H_4)](BAr$_F$) (4d). In the glovebox, a vial was charged with 53 mg (0.157 mmol, 1.14 equiv) of **3a** and 1 mL of CH_2Cl_2. The solution was cooled to −45 °C in a cold well, and 146 mg (0.137 mmol, 1.00 equiv) of TlBAr$_F$ was added to the pale yellow solution with white precipitate. The mixture was shaken for several minutes at −45 °C and was then warmed to room temperature and allowed to sit overnight; the solution was then filtered through a 2 mL medium-porosity frit, and solvent was removed from the maroon solution, leaving a viscous red oil. ^{31}P{^{1}H} NMR (δ, in CD_2Cl_2/C_6D_6, 25 °C): 225.7. ^{1}H NMR (δ, in CD_2Cl_2/C_6D_6): 3.81 (s, 6H, OCH_3), 4.28 (d, J = 4.7 Hz, NCH_2), 6.93 (d, J = 9.0 Hz, 4H, C_6H_4), 7.12 (d, J = 8.6 Hz, 4H, C_6H_4), 7.56 (s, 4H, B[(3,5-CF_3)$_2$-C_6H_3]$_4$), 7.76 (s, 8H, B[(3,5-CF_3)$_2$-C_6H_3]$_4$).

[PN(2,4,6-Me$_3$-C_6H_2)CH$_2$CH$_2$N(2,4,6-Me$_3$-C_6H_2)](BAr$_F$) (4e). A NMR tube was charged with 29 mg (0.081 mmol, 1.21 equiv) of **3b** and 71 mg (0.067 mmol, 1.00 equiv) of TlBAr$_F$. Deuteriochloroform (0.4 mL), previously cooled to −15 °C, was added to the two solids, affording a bright yellow solution with finely divided white solid. The mixture was then allowed to sit at room temperature overnight; subsequent proton NMR spectroscopy indicated the complete consumption of **3b**. TlCl could then be removed by filtration of the solution through a medium-porosity filter frit. ^{31}P{^{1}H} NMR (δ, in $CDCl_3$): 257.3. ^{1}H NMR (δ, in $CDCl_3$): 2.32 (s, 18H, coincidentally degenerate 2,4,6-(CH_3)$_3$), 4.27 (d, J = 3.9 Hz, 4H, NCH_2), 7.03 (s, 4H, C_6H_2), 7.55 (s, 4H, B[(3,5-CF_3)$_2$-C_6H_3]$_4$), 7.75 (s, 8H, B[(3,5-CF_3)$_2$-C_6H_3]$_4$).

{(PMe$_3$)[PN(4-MeO-C_6H_4)CH$_2$CH$_2$N(4-MeO-C_6H_4)]}-(OTf) (5a). In the glovebox, a NMR tube was charged with 29 mg (0.064 mmol, 1.00 equiv) of **4a** and 0.4 mL of $CDCl_3$. Trimethylphosphine (1.0 M in toluene, 0.075 mL, 0.075 mmol, 1.18 equiv) was syringed into the clear, bright orange solution; the orange color disappeared immediately upon addition of PMe_3, giving a clear, colorless solution upon mixing. ^{31}P NMR spectroscopy on the crude reaction mixture indicated that all of the **4a** had been consumed within 15 min at room temperature. The tube was then brought back into the glovebox, the volatiles were removed, and the resulting pale yellow solid was dried in vacuo. ^{31}P{^{1}H} NMR (δ, in CD_2Cl_2, 25 °C): 2.57 (br, P(CH$_3$)$_3$), 114.28 (br, PN(4-CH$_3$O-C_6H_4)(CH$_2$CH$_2$N(4-CH$_3$O-C_6H_4)). ^{1}H NMR (δ, in CD_2Cl_2): 1.62 (d, J_{P-H} = 12.5 Hz, 9 H, P(CH_3)$_3$), 3.78 (s, 6H, OCH_3), 3.97 (br, 4H, NCH_2), 6.94 (br, 4H, C_6H_4), 7.14 (br, 4H, C_6H_4).

{(PMe$_3$)[PN(2,4,6-Me$_3$-C$_6$H$_2$)CH$_2$CH$_2$N(2,4,6-Me$_3$-C$_6$H$_2$)]}(OTf) (5b). A screw-top NMR tube was charged with 28 mg (0.058 mmol, 1.00 equiv) of **4b** and 0.4 mL of $CDCl_3$. Trimethylphosphine (1.0 M in toluene, 0.070 mL, 0.070 mmol, 1.20 equiv) was syringed into the pale yellow solution, affording immediately upon shaking a clear, colorless solution. ^{31}P NMR spectroscopy indicated that all of the starting materials had been consumed within 15 min. Volatiles were removed in vacuo, yielding a pale yellow solid. $^{31}P\{^1H\}$ NMR (δ, in CD_2Cl_2, 25 °C): −10.4 (br, $P(CH_3)_3$), 144.7 (br, PN[2,4,6-$(CH_3)_3$-C_6H_2]CH_2CH_2N[2,4,6-$(CH_3)_3$-C_6H_2]).

((PMe$_3$){PN[2,6-(CHMe$_2$)$_2$-C$_6$H$_3$]CH$_2$CH$_2$N[2,6-(CHMe$_2$)$_2$-C$_6$H$_3$]})(OTf) (5c). A 50 mL round-bottom flask equipped with a magnetic stir bar was charged with 306 mg (0.548 mmol, 1.00 equiv) of **4c** and 10 mL of toluene. Trimethylphosphine (1.0 M in toluene, 1.0 mL, 1.0 mmol, 1.82 equiv) was syringed dropwise into the clear golden solution, and the resulting colorless solution and white precipitate were stirred at room temperature for 3 h. The precipitate was isolated by filtration and dried in vacuo, yielding 257 mg of white solid (0.405 mmol, 74% yield). Anal. Calcd for $C_{30}H_{47}N_2O_3P_2SF_3$: C, 56.76; H, 7.48; N, 4.41. Found: C, 52.50, 53.09, 53.06; H, 7.75, 7.78, 7.65; N, 3.96, 4.09, 3.96. $^{31}P\{^1H\}$ NMR (δ, in CD_2Cl_2, 25 °C): −17.1 (br, $P(CH_3)_3$), 153.1 (br, PN{2,6-[$CH(CH_3)_2$]$_2$-C_6H_3}CH_2CH_2N{2,6-[$CH(CH_3)_2$]$_2$-C_6H_3}). ^{1}H NMR (δ, in CD_2Cl_2, 25 °C): 1.32 (d, J = 6.6 Hz, 12H, CH(CH_3)$_2$), 1.38 (d, J = 6.8 Hz, 12H, CH(CH_3)$_2$), 1.54 (d, J_{P-H} = 10.0 Hz, 9H, P(CH_3)$_3$), 3.22 (sept, J = 6.6 Hz, 4H, CH(CH$_3$)$_2$), 3.87 (s, 4H, NCH_2), 7.28 (m, 4H, C$_6H_3$), 7.40 (m, 4H, C$_6H_3$).

{(PMe$_3$)[PN(2,4,6-Me$_3$-C$_6$H$_2$)CH$_2$CH$_2$N(2,4,6-Me$_3$-C$_6$H$_2$)]}(BAr$_F$) (5d). A solution of 0.067 mmol of **4e** in 0.4 mL of $CDCl_3$ was placed in an NMR tube, and trimethylphosphine (0.07 mL, 1.0 M in toluene, 0.07 mmol, 1.05 equiv) was added dropwise to the clear yellow solution. After the NMR tube was allowed to stand overnight, volatiles were removed from the clear, yellow solution in vacuo, affording a light yellow solid. $^{31}P\{^1H\}$ NMR (δ, in CD_2Cl_2, 25 °C): −15.0 (br, $P(CH_3)_3$), 151.8 (br, PN[2,4,6-$(CH_3)_3$-C_6H_2]CH_2CH_2N[2,4,6-$(CH_3)_3$-C_6H_2]). ^{1}H NMR (δ, in CD_2Cl_2, 25 °C): 1.55 (br, 9H, P(CH_3)$_3$), 2.30 (s, 6H, 2,4,6-(CH_3)$_3$-C$_6$H$_2$), 2.40 (s, 12H, 2,4,6-(CH_3)$_3$-C$_6$H$_2$), 3.84 (br, 4H, NCH_2), 7.00 (s, 4H, 2,4,6-$(CH_3)_3$-C$_6H_2$), 7.61 (s, 4H, B[(3,5-CF_3)$_2$-C$_6H_3$]$_4$), 7.78 (s, 8H, B[(3,5-CF_3)$_2$-C$_6H_3$]$_4$).

{*trans*-RhCl(PPh$_3$)$_2$[PN(4-MeO-C$_6$H$_4$)CH$_2$CH$_2$N(4-MeO-C$_6$H$_4$)]}(OTf) (6). A CH_2Cl_2 (20 mL) solution of $RhCl(PPh_3)_3$ (660 mg, 0.713 mmol) was cooled to −50 °C, to which solid **4a** (321 mg, 0.712 mmol, 1.00 equiv) was added slowly. The solution was warmed to room temperature and was stirred for an additional 60 min at 25 °C. After removal of volatiles, the resulting solid was washed three times with 10 mL portions of toluene and was dried in vacuo, yielding 635 mg of a bright orange powder, **6** (0.571 mmol, 80% yield). Anal. Calcd for $C_{53}H_{48}N_2O_5P_3SF_3RhCl$: C, 57.17; H, 4.35; N, 2.52. Found: C, 56.54, 56.72, 56.27; H, 4.51, 4.50, 4.45; N, 2.42, 2.40, 2.41. ^{1}H NMR (δ, in $CDCl_3$): 3.75 (d, 7.1 Hz, 4H, NCH_2), 3.86 (s, 6H, OCH_3), 6.78 (d, 8.8 Hz, 4H, C$_6H_4$), 7.38, 7.40, 7.41 (overlapping multiplets, 28H, C$_6H_4$ and C$_6H_5$), 7.51 (m, J = 4.4 Hz, 6H, C$_6H_5$). $^{13}C\{^1H\}$ NMR (δ, in $CDCl_3$): 50.15 (s, NCH_2), 55.73 (s, OCH_3), 114.31 (s, C$_6$H$_4$), 119.96 (m, overlaps with Ph resonances, $^1J_{C-F}$ = 323 Hz, OSO_2CF_3), 121.93 (d, J_{P-C} = 7.6 Hz, C$_6$H$_4$), 128.72 (m, J = 5.3 Hz, C$_6$H$_5$), 130.18 (d, J = 11.1 Hz, C$_6$H$_4$), 131.34 (s, C$_6$H$_5$), 131.99 (m, J = 24.8, C$_6$H$_5$), 133.87 (m, J = 6.0 Hz, C$_6$H$_5$), 158.88 (s, C$_6$H$_4$). $^{31}P\{^1H\}$ NMR (δ, in $CDCl_3$): 24.91 (dd, $^1J_{Rh-P}$ = 102 Hz, $^2J_{P-P}$ = 51 Hz, PPh$_3$), 240.18 (dt, $^1J_{Rh-P}$ = 311 Hz, $^2J_{P-P}$ = 51 Hz, N$_2P$).

Reaction of 4b,c with RhCl(PPh$_3$)$_3$. An NMR tube was charged with approximately 0.04 mmol of the appropriate phosphenium (**4**) and 1.0 equiv of $RhCl(PPh_3)_3$, to which $CDCl_3$ (0.4 mL) was added at room temperature. The crude reaction mixtures were then analyzed by ^{1}H and ^{31}P NMR spectroscopy. No attempts were made to isolate or further characterize either the *cis* or *trans* isomers of **7** due to the mixture of products resulting from **4b**/$RhCl(PPh_3)_3$.

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Supporting Information Available: ^{1}H NMR spectra for **1a**−**c**, **2a**−**c**, **3a**−**c**, and **4a**−**c**, as well as tables of atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for **5c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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