An Unusual Equilibrium Chlorine Atom Transfer Process and Its Potential for Assessment of Steric Pressure by Bulky Aryls

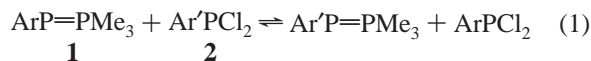Rhett C. Smith, Shashin Shah, Eugenijus Urnezius, and John D. Protasiewicz*

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Sterically demanding aryls and alkyls have enjoyed great success in a wide spectrum of applications. In particular, the bulky aryl Mes* $(2,4,6\text{-}^tBu_3C_6H_2)$ has been extensively employed since its pioneering use for stabilizing the first diphosphene.[1] The *ortho-tert*-butyl groups of this aryl with concomitant close CH contacts can lead to steric pressures and novel reactivity for directly attached functional groups. For example, zirconium phosphanido complexes bearing Mes* undergo surprisingly facile P−C bond cleavage.[2] The strain imposed by Mes* has also been identified as a thermodynamic driving force promoting formation of iminopnictines and an iodoselenide.[3] More recently, there has been much interest in the use of sterically encumbered *meta*-terphenyls $(2,6\text{-}Ar_2C_6H_3)$ for accessing novel element−element multiple bonds, interesting molecular geometries and coordination environments, and models of biological systems.[4] These aryls place a steric wall at a greater distance from a reactive center and thus provide steric protection comparable to the Mes* group without suffering reactions driven by steric *pressure*. A fundamental question for these, and other sterically demanding units, is the issue of quantifying and dissecting the overall steric properties. While in some cases structural data may allow qualitative comparisons,[5] simple general methods are lacking. Herein we present details of an unprecedented equilibrium chlorine atom exchange reaction involving phosphanylidene-σ^4-phosphoranes[6] ArP=PR$_3$ bearing sterically encumbered aryls and the use of this process as a systematic means to assess steric *pressure* imposed by bulky aryls.

We have reported the synthesis and characterization of stable phosphanylidene-σ^4-phosphoranes such as Mes*P=PMe$_3$ (**1a**) and $2,6\text{-}Mes_2C_6H_3P=PMe_3$ (**1b**).[7] These useful materials act as phospha-Wittig reagents upon reaction with aldehydes and as precursors to highly reactive phosphinidenes.[8] During our studies, it was discovered that these two materials undergo rapid chlorine atom exchange with ArPCl$_2$ in solution. Thus, mixing Mes*PCl$_2$ (**2a**) and **1b** in C$_6$D$_6$ at room temperature results in rapid (<5 min) equilibration to a mixture of **1b**, **2a**, $2,6\text{-}Mes_2C_6H_3PCl_2$ (**2b**), and

$$\text{ArP=PMe}_3 + \text{Ar}'\text{PCl}_2 \rightleftharpoons \text{Ar}'\text{P=PMe}_3 + \text{ArPCl}_2 \quad (1)$$
$$\mathbf{1} \qquad\qquad\quad \mathbf{2}$$

1a, as indicated in eq 1. An estimate of $K_{eq} \geq 190$ was established using ^{1}H NMR integration and an internal standard. Consistent with this estimated equilibrium value, a solution prepared from pure **2b** and **1a** showed little or no evidence of net exchange on the same time scale.

While the reaction between **2a** and **1b** is rapid, the spectra show no evidence for line broadening, indicating that the exchange process is slow on the NMR time scale. Monitoring solutions on much longer time scales (hours) leads to the observation of signals for complicated mixtures of all three possible dichlorodiphosphines of the form Ar(Cl)PP(Cl)Ar. The reaction of **1b** and **2b** over 1−2 h provided one of these materials, ArP(Cl)P(Cl)Ar (**3**, Ar = 2,6-
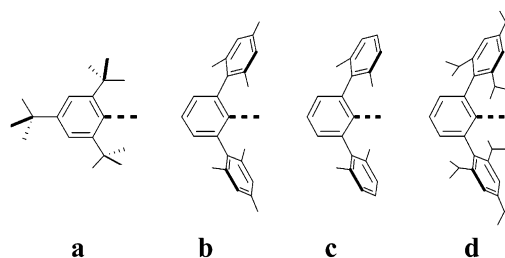
Chart 1

| a | b | c | d |

Table 1. Thermodynamic Data Obtained for a Series of Reaction Partners^a

| Ar	Ar′	K_{eq}, eq 1	Ar	Ar′	ΔH_{rxn}, eq 3 (kcal/mol)
2a	**1b**	≥ 190	**2a**	**5b**	−13.2
2a	**1d**	≥ 140	**2a**	**5d**	−9.7
2b	**1c**	$1, 1^b$	**2b**	**5c**	0.2
2d	**1c**	$20\ (18)^b$	**2d**	**5c**	−3.4

^{a} Numbers in parentheses determined by reaction of **2c** and **1d**. ^{b} Reaction was catalyzed by added PMe$_3$.

Mes$_2$C$_6$H$_3$), in modest yields.[9] Compound **3** does not readily participate in chlorine atom transfer reactions.

This atom transfer process was then extended to include two other commonly used terphenyls with varying steric properties (Chart 1). These studies showed that the atom transfer process was indeed general. The rates, however, varied greatly, as did the position of equilibrium shown in eq 1. Rates for the exchange process were too slow in some cases to compete with the slow thermal decomposition of ArP=PMe$_3$. Fortunately, our efforts to delineate the mechanism of the atom transfer resulted in the discovery that PMe$_3$ acts as a catalyst for eq 1. For example, addition of 2 equiv of PMe$_3$ to a NMR tube of **1c** and **2b** results in a dramatic reduction of the time for equilibration, from 16 h to 10 min (without impacting the final K_{eq}). Thus, for slow reactions, PMe$_3$ was used to catalyze the atom transfer reaction. The equilibrium constants obtained for a series of reaction partners are listed in the left side of Table 1.

Analysis of these data reveals several interesting facts. First, for systems having a close steric similarity about the phosphorus centers (**b** and **c**), the equilibrium constant K_{eq} is one within experimental error. For atoms shielded by terphenyl units, the immediate steric pressure placed upon the attached atom by the aryl is largely defined by the ortho-substituents on the outer aromatic rings. Second, the Mes*P group appears to have the greatest desire to rid itself of two chlorine atoms of any of the aryls studied.

One hypothesis to account for the equilibria portrayed by eq 1 is that the aromatic group that places the greatest steric pressure on the directly attached phosphorus atom will show a greater tendency to host fewer attached groups at this center. This important point (thermodynamic) should not be confused with the more

Scheme 1. Proposed Mechanism for the PMe$_3$-Promoted Chlorine Atom Transfer Process
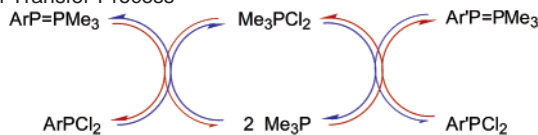

commonly discussed ability of such groups to render so-called kinetic stabilization to reactive multiply bonded units (for which other factors are also important, such as thermodynamic destabilization of cycloaddition products[3c]). Using this simple assumption, one can estimate the relative penalties for accommodating a PCl$_2$ functional group onto the series of hindered aryls by calculating values of ΔH_{rxn} (eq 2 and Table 1, right) for related fictional H/PCl2 exchanges.[10] A rough correlation exists, and, impressively, the Mes*

$$\underset{\mathbf{2}}{ArPCl_2} + \underset{\mathbf{5}}{Ar'H} \rightleftharpoons ArH + Ar'PCl_2 \qquad (2)$$

unit is maximally effective at destabilizing a three-coordinate phosphorus center as compared to all other aryls used in this study, even terphenyl **d**.

Two novel electronic effects specific for terphenyls might influence these equilibria. Through-space interactions of the outer aryl π-system with the PCl$_2$ unit are possible.[11] A preliminary determination of $K_{eq} = 1$ for the reaction of 2,6-(2,6-Cl$_2$C$_6$H$_3$)$_2$C$_6$H$_3$-PCl$_2$ (a terphenyl that is nearly isosteric to **c**, but electronically different) and **1c** suggests that this effect is negligible.[12] Menshutkin interactions have been suggested in the structures of 2,6-Ar$_2$C$_6$H$_3$-EX$_2$ (E = P, As, Sb, and Bi) on the basis of the disparity in the C$_{ortho}$–C$_{ipso}$–E angles and a close approach of the pnictogen to one of the two ortho aromatic rings.[13] While our minimized structures for 2,6-Ar$_2$C$_6$H$_3$PCl$_2$ consistently reproduce these geometrical distortions, they also suggest that the closer approach of the phosphorus atom to one ring is actually an artifact of the repulsive forces between the two halogens and the opposite aromatic ring. This hypothesis is corroborated by the finding that the phosphorus atoms are actually deflected away from the aromatic rings in minimized structures of 2-ArC$_6$H$_4$PCl$_2$.[10]

The finding that PMe$_3$ catalyzes the chlorine atom transfer leads to the mechanism proposed in Scheme 1. Consistent with the mechanism is the fact that ArP=PMe$_3$ can be prepared by action of excess PMe$_3$ upon ArPCl$_2$, although the process is somewhat inefficient without Zn dust to drive the equilibrium to the right (eq 3) by forming ZnCl$_2$. Trialkylphosphines are well-known agents

$$ArPCl_2 + xs\ PMe_3 \rightleftharpoons ArP{=}PMe_3 + Me_3PCl_2 \qquad (3)$$
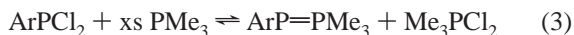
for dehalogenation of halophosphines.[14] Traces of PMe$_3$ in these solutions might arise from the known slow thermal degradation of ArP=PMe$_3$. The catalytic efficacy of the relatively small PMe$_3$ obviates the need for approach of two phosphorus centers bearing hindered aryls. Scheme 1 predicts that reaction of **1c** and **2b** should also be catalyzed by addition of Me$_3$PCl$_2$, but in this case the

extreme insolubility of the independently prepared and isolated reagent thwarted any catalytic behavior. The more soluble material ^{n}Bu$_3$PCl$_2$, however, is indeed an efficient catalyst.

The reactions we report here represent interesting main group versions of related chlorine atom transfer reactions between transition metal centers that have received some attention. In fact, some of these systems exchange phosphine ligands *and* chlorine atoms and thus suggest the potential *catalytic* role of phosphines in other chlorine atom transfer processes.[15] Extensions of the method here to other sterically encumbered aryls and alkyls should allow a rapid means (^{31}P NMR spectroscopy) to determine the relative impact of bulky groups at main group centers and to begin the more challenging task of unraveling presumed electronic effects that may be overshadowed by dominating steric forces.

Supporting Information Available: Experimental and computational details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) (a) Compound **3**: ^{31}P NMR δ 71.6 (Mes* derivative δ 75.7 ppm). Full data for **3**, see Supporting Information. (b) Data for Mes* derivative, see: Goldwhite, H.; Kaminski, J.; Millhauser, G.; Ortiz, J.; Vargas, M.; Vertal, L.; Lappert, M. F.; Smith, S. J. *J. Organomet. Chem.* **1986**, *310*, 21−25.
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