reduction of purified **6** in the dark at −78 °C with 1 equiv of $K[2,6\text{-}C_{10}H_6{}^tBu_2]$ and subsequent [PPN]Cl metathesis gives $[PPN]_2$**2** in 22% yield, suggesting that $\mathbf{2}^{2-}$ may be formed via a diradical intermediate such as $\mathbf{7}^{2-}$, in which a single C–C bond links the monomer units.

The formation of $\mathbf{2}^{2-}$ from $\mathbf{3}^+$ is of interest within the context of benzene dimerization and of the ability of a transition-metal center to promote this reaction. The reaction also, however, has wider implications for the potential existence of a broad range of other cycloaddition reactions[10] of coordinated arenes in both the chromium and manganese systems, and experiments exploring these possibilities are underway in our laboratories together with detailed mechanistic studies.

Acknowledgment. We thank the National Science Foundation for financial support through CHE-8722424 and Professor Maurice Brookhart for helpful conversations.

Registry No. $\mathbf{1}^-$, 136115-43-0; [PPN]**2**, 136115-45-2; $\mathbf{3}^+$, 41656-02-4; **5**, 12108-14-4; **6**, 136115-46-3; $[Mn(\eta^4\text{-}C_{10}H_8)(CO)_3]^-$, 131130-38-6.

Supplementary Material Available: Spectroscopic and analytical data for [PPN]**2** and **6**, crystal data for [PPN]**2**, and tables of atomic coordinates, bond lengths and angles, anisotropic displacement coefficients, and H atom positional and displacement parameters for [PPN]**2** (6 pages); tables of structure factors for [PPN]**2** (21 pages). Ordering information is given on any current masthead page.

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(13) Gaudet, M. V.; Hanson, A. W.; White, P. S.; Zaworotko, M. J. *Organometallics* **1989**, *8*, 286.

Metal Complexes of the Bridging Bidentate Metallophosphine Ligand, $[Fe_3(CO)_9(\mu_3\text{-}P)_2]^{2-}$

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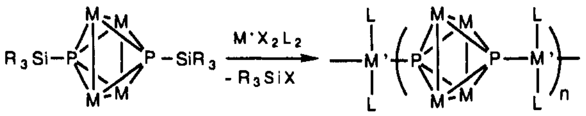
Bicapped phosphinidene clusters form an extensively studied class of compounds that have drawn both chemical and theoretical attention due to their interesting structures, their facile redox chemistry, and their coordinative unsaturation.[1] We are exploring chemistry that will enable incorporation of the versatile bicapped $M_x(CO)_y(\mu_x\text{-}P)_2$ unit (x = 3, 4) into an extended array with the potential of cooperative interaction among the clusters by exploiting the coordinating ability of the cluster-bound phosphorus atoms (see II).[2] The strategy being employed to synthesize the chains involves preparation of bicapped silylphosphinidene clusters (for example, I), followed by removal of the silyl group in condensation reactions between the bicapped clusters and metal dihalide complexes (eq 1).[3] We report here preliminary investigations toward this goal involving reactions of the bifunctional cluster, $(\mu_2\text{-}H)Fe_3(CO)_9[\mu_2\text{-}P(H)SiMe_3](\mu_3\text{-}PSiMe_3)$ (**1**), with metal monohalides belonging to the family $(C_5R_5)Fe(CO)_2X$ (R = Me, X = Cl; R = H, X = Cl, I) to selectively produce discrete metal complexes of the bridging bidentate metallophosphine ligand, $[Fe_3(CO)_9(\mu_3\text{-}P)_2]^{2-}$. This study lays the foundation for the chemistry to *rationally* prepare extended cluster chains.



(1)

I II

The cluster, $(\mu_2\text{-}H)Fe_3(CO)_9[\mu_2\text{-}P(H)SiMe_3](\mu_3\text{-}PSiMe_3)$ (**1**), is prepared as the primary product upon warming a hexanes/*cis*-cyclooctene reaction mixture containing 2 equiv of PH_2SiMe_3 and 3 equiv of $Fe(CO)_3(\textit{cis}\text{-cyclooctene})_2$[4] from −40 °C to room temperature.[5] Due to the difficulties encountered in chromatographic purification of complexes containing readily hydrolyzed $P\text{–}SiMe_3$ linkages, reactions of spectroscopically determined molar quantities of **1** with metal halides are performed in situ.

Stirring a solution of **1** and excess $CpFe(CO)_2Cl$ (Cp = $\eta^5\text{-}C_5H_5$) in benzene over a period of 1 day results in desilylation of the cluster[6] concomitant with rearrangement to the $Fe_3(\mu_3\text{-}P)_2$ core to produce the disubstituted cluster, $Fe_3(CO)_9[\mu_3\text{-}PFe(CO)_2Cp]_2$ (**2**) (Scheme I).[7] The structure of **2**, as established by a single-crystal X-ray diffraction study (Figure 1a),[8] consists of an open Fe_3 triangle, with only two Fe–Fe bonds (like **1**), which is capped on each face by a triply bridging $PFe(CO)_2Cp$ unit. The phosphorus atoms are bound nearly equidistantly to the Fe_3-cluster iron atoms (Fe(cluster)–P = 2.25 (1) Å) and the capping iron atoms (Fe(cap)–P = 2.262 (6) Å). The isostructural phenylphosphinidene cluster, $Fe_3(CO)_9(\mu_3\text{-}PPh)_2$,[9] has shorter Fe–P bonds (Fe–P(av) = 2.218 (5) Å), which result in a much shorter P···P nonbonding distance for the phenyl-capped cluster (2.587 (5) Å) than for **2** (2.725 (6) Å).

The reactivity of the silyl cluster **1** toward the halides, $CpFe(CO)_2X$, depends on the identity of X, as well as the substituents on the Cp ring. Excesses of $CpFe(CO)_2I$ and $(C_5Me_5)Fe(CO)_2Cl$ do not react with **1** in benzene solution over a period of several days; however, reaction can be initiated by adding a stoichiometric amount of water into the reaction mixture to generate a mixture of the hydrolyzed clusters, $Fe_3(CO)_9(\mu_3\text{-}PH)_2$ and $(\mu_2\text{-}H)Fe_3(CO)_9(\mu_2\text{-}PH_2)(\mu_3\text{-}PH)$.[10] Reaction between the halides and the hydrolyzed clusters occurs over 1 day, to produce the monosubstituted clusters, $Fe_3(CO)_9[\mu_3\text{-}PFe(CO)_2Cp'](\mu_3\text{-}PH)$ (**3a**, Cp′ = C_5H_5; **3b**, Cp′ = C_5Me_5),[11] as the principle products. The above

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(1) See, for example: (a) Huttner, G.; Knoll, K. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 743. (b) Halet, J.-F.; Hoffmann, R.; Saillard, J.-Y. *Inorg. Chem.* **1985**, *24*, 1695. (c) Ohst, H. H.; Kochi, J. K. *Inorg. Chem.* **1986**, *25*, 2066. (d) Jaeger, J. T.; Vahrenkamp, H. *Organometallics* **1988**, *7*, 1746. (e) Jaeger, J. T.; Field, J. S.; Collison, D.; Speck, G. P.; Peake, B. M.; Hähnle, J.; Vahrenkamp, H. *Organometallics* **1988**, *7*, 1753.

(2) Direct intercluster coordination by cluster-bound phosphorus, arsenic, and sulfur to yield cyclic cluster trimers has been observed. Vizi-Orosz, A.; Galamb, V.; Palyi, G.; Marko, L. *J. Organomet. Chem.* **1976**, *111*, 61. Adams, R. D.; Maennig, D.; Segmueller, B. E. *Organometallics* **1983**, *2*, 149.

(3) Reactions of silylphosphines $(SiMe_3)_2PR$ and $(SiMe_3)PR_2$ with metal halides have been utilized to prepare phosphido bridged complexes and phosphinidene capped clusters. See, for example: (a) Fenske, D. M.; Ohmer, J.; Hachgenei, J.; Merzweiler, K. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1277. (b) Schäfer, H.; Zipfel, J.; Gutekunst, B.; Lemmert, U. *Z. Anorg. Allg. Chem.* **1985**, *529*, 157.

(4) Fleckner, H.; Grevels, F. W.; Hess, D. *J. Am. Chem. Soc.* **1984**, *106*, 2027.

(5) Bautista, M.; White, P.; Schauer, C. K., manuscript in preparation. See supplementary material.

(6) Observation of this reaction by ^1H NMR spectroscopy in benzene-d_6 solution shows Me_3SiCl to be the primary silicon product.

(7) Following chromatography, crystallization from CH_2Cl_2/pentane yielded orange-red crystals of **2** (60 mg, 70%). ^{31}P NMR (δ, ppm, C_6H_6): 476 (s). ^1H NMR (δ, ppm, C_6D_6): 4.32 (d, $^3J(H,P)$ = 4 Hz, C_5H_5). IR (ν_{CO}, cm^{-1}, Et_2O): 2061 (w), 2037 (m), 2019 (s), 1993 (m), 1967 (m), 1948 (w). Satisfactory C and H analyses were obtained.

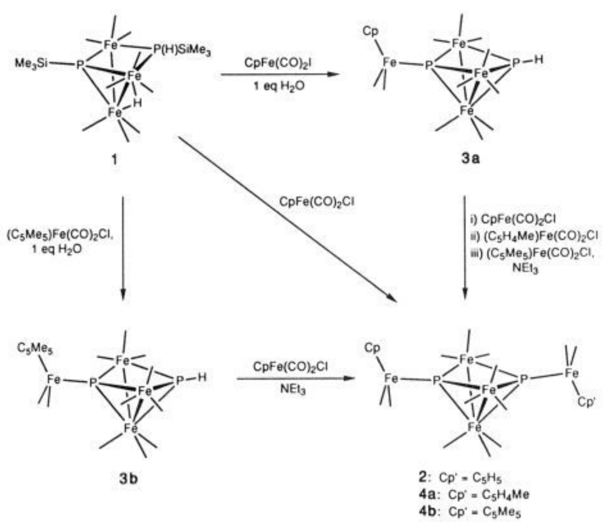
(8) For $\mathbf{2}\cdot C_6H_6$ ($C_{29}H_{16}Fe_5O_{13}P_2$): a = 12.839 (9) Å, b = 14.663 (8) Å, c = 18.001 (12) Å, β = 107.00 (6)°, at −100 °C. Space group $P2_1/c$ (Z = 4). Data collection on an Enraf-Nonius CAD4 diffractometer yielded 2647 unique observed ($I \geq 2.5\sigma(I)$) reflections. Least-squares refinement of 443 parameters converged at R (R_w) = 0.063 (0.088), GOF = 2.31.

(9) Cook, S. L.; Evans, J.; Gray, L. R.; Webster, M. *J. Organomet. Chem.* **1982**, *236*, 367.

(10) A ^{31}P NMR spectrum taken immediately after addition of H_2O shows conversion of **1** to $Fe_3(CO)_9(\mu_3\text{-}PH)_2$ and $(\mu_2\text{-}H)Fe_3(CO)_9(\mu_2\text{-}PH_2)(\mu_3\text{-}PH)$ (combined spectroscopic yield by ^{31}P NMR spectroscopy, 60%). We have not yet been able to successfully chromatograph and isolate the hydrolyzed clusters. $Fe_3(CO)_9(\mu_3\text{-}PH)_2$: ^{31}P NMR (δ, C_6H_6, ppm) 234 (AA′XX′, $^1J(H,P)$ = 315 Hz, $^3J(H,P)$ = 15 Hz, $^2J(P,P)$ = 346 Hz). Coupling constants obtained by simulation of the spectrum with LAOCN5 (Quantum Chemistry Program Exchange, No. QCMP 049). $(\mu_2\text{-}H)Fe_3(CO)_9(\mu_2\text{-}PH_2)(\mu_3\text{-}PH)$: ^{31}P NMR (δ, C_6H_6, ppm) 215 (ddm, $^1J(H,P)$ = 337 Hz, $^2J(P,P)$ = 248 Hz, $\mu_3\text{-}PH$), −184 (dtm, $^1J(H,P)$ = 325 Hz, $^2J(P,P)$ = 248 Hz, $\mu_2\text{-}PH_2$).

0002-7863/91/1513-8963$02.50/0

Scheme I



reactions illustrate that the hydrolyzed clusters are more reactive to metal halides than the silyl cluster. Furthermore, the substitution of one phosphorus site by a CpFe(CO)$_2$ group significantly reduces the reactivity of the remaining P–H bond, enabling synthesis of the monosubstituted clusters. Attempts to prepare the hydrolyzed clusters directly from reaction of Fe(CO)$_3$(*cis*-cyclooctene)$_2$ and PH$_3$ were unsuccessful.

The reaction of the monosubstituted clusters with other metal halide complexes provides a route to the rational synthesis of disubstituted clusters with two different substituents on the phosphorus atoms. As in the desilylation reactions of **1**, the rates of reaction of **3a** with metal halide complexes depend on the metal halide. A 5-fold molar excess of (C$_5$H$_4$Me)Fe(CO)$_2$Cl and **3a** react in benzene solution over 1 day to produce the asymmetric cluster, Fe$_3$(CO)$_9$[μ_3-PFe(CO)$_2$Cp][μ_3-PFe(CO)$_2$(C$_5$H$_4$Me)] (**4a**) as the primary product.[12] In contrast, no reaction between **3a** and excess (C$_5$Me$_5$)Fe(CO)$_2$Cl occurs under identical reaction conditions. Addition of NEt$_3$[13] (~6 equiv) accelerates the (C$_5$Me$_5$)Fe(CO)$_2$Cl reaction, which goes to completion within 15 min to produce Fe$_3$(CO)$_9$[μ_3-PFe(CO)$_2$Cp][μ_3-PFe(CO)$_2$(C$_5$Me$_5$)] (**4b**).[14] The structure of **4b** was confirmed by a single-crystal X-ray diffraction study (Figure 1b),[15] which clearly shows the two different capping complexes. The bulky C$_5$Me$_5$ group is oriented toward the open Fe···Fe edge. There are no significant structural differences between **2** and **4b**.

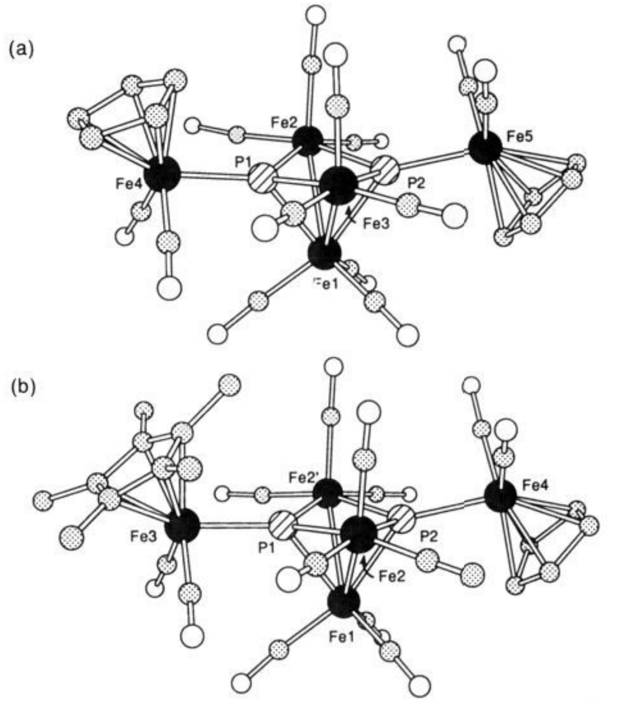


Figure 1. (a) Ball and stick drawing of the molecular structure of **2**. Selected distances (Å): Fe1–Fe2 = 2.704 (3), Fe1–Fe3 = 2.718 (4), Fe2···Fe3 = 3.538 (3), P1···P2 = 2.725 (6), Fe1–P1 = 2.259 (5), Fe1–P2 = 2.266 (4), Fe2–P1 = 2.234 (4), Fe2–P2 = 2.255 (5), Fe3–P1 = 2.240 (4), Fe3–P2 = 2.258 (5), Fe4–P1 = 2.257 (5), Fe5–P2 = 2.266 (5). (b) Ball and stick drawing of one of the two independent molecules of *m* symmetry in the crystal structure of **4b**. Selected distances (Å) (distances for the second independent molecule are given in parentheses): Fe1–Fe2 (Fe5–Fe6) = 2.693 (3) (2.687 (3)), Fe2···Fe2′ (Fe6···Fe6′) = 3.578 (4) (3.546 (4)), P1···P2 (P3···P4) = 2.704 (6) (2.742 (7)), Fe1–P1 (Fe5–P3) = 2.280 (5) (2.289 (5)), Fe1–P2 (Fe5–P4) = 2.267 (5) (2.258 (5)), Fe2–P1 (Fe6–P3) = 2.263 (3) (2.264 (3)), Fe2–P2 (Fe6–P4) = 2.237 (3) (2.238 (3)), Fe3–P1 (Fe7–P3) = 2.292 (5) (2.313 (5)), Fe4–P2 (Fe8–P4) = 2.279 (5) (2.288 (5)).

The capping metal complex in the monosubstituted cluster plays a role in the P–H bond reactivity. The clusters **3a** and **3b** display very different reactivity toward CpFe(CO)$_2$Cl. The disubstituted cluster **2** is produced in 1 day by reaction of a benzene solution of **3a** with a 5-fold molar excess of CpFe(CO)$_2$Cl, while very little reaction (~5%) occurs between **3b** and CpFe(CO)$_2$Cl under identical conditions.[16] The P–H stretching frequency in **3b** (2298 cm^{-1}) is slightly higher in energy than that in **3a** (2294 cm^{-1}), suggesting that a stronger P–H bond for **3b** may, in part, account for this observed difference in reactivity.

Several key features of the reaction between cluster-bound P–H and P–Si bonds and metal halides have been delineated. With the appropriate choice of reactants and reaction conditions, monosubstituted, disubstituted, and asymmetric disubstituted clusters can be obtained as the principle products. The monosubstituted clusters will be of particular value as "end groups" of a chain, and studies are in progress directed toward the stepwise synthesis of cluster oligomers employing cleavage reactions with bifunctional metal halides.

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(11) **3a**: spectroscopic yield by ^{31}P NMR spectroscopy, 50% based on **1**; low-temperature chromatography yielded **3a** as an orange band; solutions of **3a** partially decompose upon removal of the solvent, and we were unable to isolate **3a** as a pure solid; ^{31}P NMR (δ, ppm, C_6H_6) 445 (dd, ^2J(P,P) = 232 Hz, ^3J(H,P) = 12 Hz, μ_3-*P*Fe(CO)$_2$Cp), 270 (dd, ^2J(P,P) = 232 Hz, ^1J(H,P) = 291 Hz, μ_3-*P*H); ^{1}H NMR (δ, ppm, C_6D_6) 5.26 (dd, 1 H, ^1J(H,P) = 291 Hz, ^3J(H,P) = 12 Hz, P*H*), 4.11 (s, 5 H, C_5H_5); IR (ν_{CO}, cm^{-1}, hexanes) 2070 (vw), 2036 (s), 2013 (m), 1991 (m), 1984 (w), 1974 (w); IR (ν_{PH}, cm^{-1}, Nujol mull) 2294 (vw). **3b**: spectroscopic yield by ^{31}P NMR spectroscopy, 50% based on **1**; low-temperature chromatography yielded **3b** as an orange band; ^{31}P NMR (δ, ppm, C_6H_6) 473 (dd, ^2J(P,P) = 213 Hz, ^3J(H,P) = 11 Hz, μ_3-*P*Fe(CO)$_2$(C$_5$Me$_5$)), 275 (dd, ^2J(P,P) = 213 Hz, ^1J(H,P) = 291 Hz, μ_3-*P*H); ^{1}H NMR (δ, ppm, C_6D_6) 5.26 (dd, 1 H, ^1J(H,P) = 291 Hz, ^3J(H,P) = 11 Hz, P*H*), 1.37 (d, 15 H, ^4J(H,P) = 0.8 Hz, C$_5$(C*H*$_3$)$_5$); IR (ν_{CO}, cm^{-1}, hexanes) 2065 (vw), 2032 (s), 2024 (m), 2009 (m), 1998 (vw), 1987 (m), 1973 (w); IR (ν_{PH}, cm^{-1}, Nujol mull) 2298 (vw). Reactions of **3a** and **3b** were performed on the chromatographed solutions without isolation.

(12) **4a**: capping group exchange reactions to form symmetrically capped clusters occur only to a small extent (<5%); following chromatography, crystallization from CH$_2$Cl$_2$/pentane yielded orange-red crystals (10 mg, 95%); ^{31}P NMR (δ, ppm, CH$_2$Cl$_2$) 477 (AB q: P$_A$, 478.1, *P*Fe(CO)$_2$(C$_5$H$_4$Me), P$_B$, 476.0 *P*Fe(CO)$_2$Cp, ^2J(P$_A$,P$_B$) = 160 Hz); ^{1}H NMR (δ, ppm, C$_6$D$_6$) 4.55 (m, 2 H, MeC$_5$*H*$_2$H′$_2$), 4.15 (m, 2 H, MeC$_5$H$_2$*H*′$_2$), 1.34 (s, 3 H, *Me*C$_5$H$_2$H′$_2$), 4.33 (d, 5 H, ^3J(H,P) = 1.4 Hz, C$_5$*H*$_5$); IR (ν_{CO}, cm^{-1}, Et$_2$O) 2059 (w), 2036 (m), 2018 (s), 1993 (m), 1967 (m), 1947 (w). Satisfactory C and H analyses were obtained.

(13) Diethylamine has been observed to accelerate the reactions of secondary phosphine complexes with metal halides. Yasufuku, K.; Yamazaki, H. *J. Organomet. Chem.* **1971**, *28*, 415.

(14) **4b**: following chromatography, crystallization from CH$_2$Cl$_2$/pentane yielded orange-red crystals (13 mg, 75%); ^{31}P NMR (δ, ppm, C$_6$D$_6$) 510 (d, ^2J(P,P) = 140 Hz, *P*Fe(CO)$_2$(C$_5$Me$_5$)), 471 (d, ^2J(P,P) = 140 Hz, *P*Fe(CO)$_2$Cp); ^{1}H NMR (δ, ppm, C$_6$D$_6$) 4.49 (d, 5 H, ^3J(H,P) = 1.4 Hz, C$_5$*H*$_5$), 1.52 (s, 15 H, C$_5$(C*H*$_3$)$_5$); IR (ν_{CO}, cm^{-1}, Et$_2$O) 2057 (w), 2030 (m), 2016 (vs), 1991 (m), 1963 (m), 1945 (vw). Satisfactory C and H analyses were obtained.

(15) For **4b** (C$_{28}$H$_{20}$Fe$_5$O$_{13}$P$_2$): a = 12.258 (3) Å, b = 15.149 (3) Å, c = 17.817 (4) Å, β = 95.16 (2)°. Space group, $P2_1/m$ (Z = 4). Data collection on a Rigaku AFC6S diffractometer yielded 2833 unique observed ($I \geq 2.5\sigma(I)$) reflections. The asymmetric unit consists of two unique molecules of *m* symmetry. Rotational disorder of the C$_5$Me$_5$ ring on one of the unique molecules was observed. Least-squares refinement of 454 parameters converged at $R(R_w)$ = 0.060 (0.066), GOF = 1.78.

(16) Reactions of **3b** and CpFe(CO)$_2$Cl are also accelerated by addition of NEt$_3$ and go to completion within 15 min after addition.

Acknowledgment. Partial financial support provided by a Presidential Young Investigator Award from the National Science Foundation (CHEM-8958027), the donors of the Petroleum Research Fund, administered by the American Chemical Society (21923-G3), the North Carolina Board of Science and Technology (89SE06), and the Department of Chemistry at the University of North Carolina at Chapel Hill is gratefully acknowledged. Partial funds for equipping the single-crystal X-ray diffraction facility at UNC-CH were provided by the National Science Foundation (CHE-8919288).

Supplementary Material Available: Details of the preparation and characterization of compounds **1**, **2**, **3a**,**b**, and **4a**,**b** and listings of complete crystallographic data and results for $Fe_3(CO)_9[\mu_3\text{-}PFe(CO)_2Cp]_2$ (**2**) and $Fe_3(CO)_9[\mu_3\text{-}PFe(CO)_2Cp][\mu_3\text{-}PFe(CO)_2(C_5Me_5)]$ (**4b**) (23 pages); listing of observed and calculated structure factors for **2** and **4b** (36 pages). Ordering information is given on any current masthead page.

Intramolecular Schmidt Reaction of Alkyl Azides

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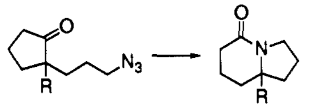
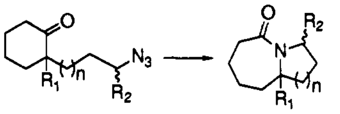
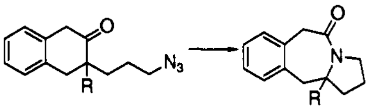
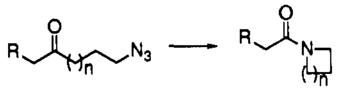
Received August 7, 1991

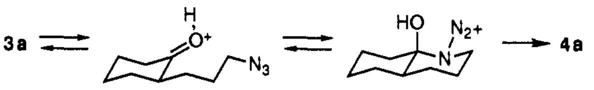
The reaction of hydrazoic acid with ketones to afford a ring-expanded lactam (the Schmidt reaction) is an important method for the preparation of nitrogen-containing heterocycles.[1] The extension of the reaction to provide N-substituted lactams would be particularly useful;[2] however, attempts to replace hydrazoic acid with alkyl azides under classical Schmidt conditions (strong acid) were generally unsuccessful.[1,3] In a series of papers in the late 1950s, Boyer and co-workers did manage to establish a narrow range of azides that react with aromatic aldehydes, but the bona fide migration of an alkyl group was not observed in any of these examples.[4,5] In addition, the intramolecular reaction of several enones with azides gave Schmidt-type products upon thermolysis, but the reaction proceeds by initial attack of the azide upon the double bond followed by rearrangement of the resulting triazoline.[6]

Table I. Intramolecular Reactions of Alkyl Azides with Ketones

entry	compounds	conditns[a]	yield, %
	 **1a,b** **2a,b**		
1	**a**, R = H	TFA, 40 min	83
2	**b**, R = CO_2Me	TFA, 16 h	66
3	**b**	$TiCl_4$, CH_2Cl_2, 20 min	70
	 **3a-d** **4a-d**		
4	**a**, R_1 = H, R_2 = H, *n* = 1	TFA, 10 min	90
5	**b**, R_1 = CO_2Et, R_2 = H, *n* = 1	TFA, 1 h	93
6	**c**, R_1 = H, R_2 = H, *n* = 2	TFA, 24 h	0
7	**c**	$TiCl_4$, CH_2Cl_2, 16 h	91
8	**d**, R_1 = H, R_2 = CH_3, *n* = 1	TFA, 20 min	74
	 **5a,b** **6a,b**		
9	**a**, R = H	TFA, 20 min	91
10	**b**, R = CH_3	TFA, 20 min	91
	 **7a,b** **8a,b**		
11	**a**, *n* = 1, R = H	TFA or $TiCl_4$	0
12	**b**, *n* = 2, R = CO_2Me	TFA, 12 h	66
13	**b**	$TiCl_4$, 15 min	64

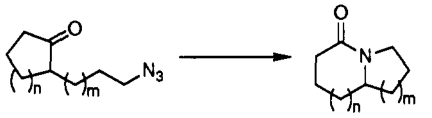
[a] All reactions were carried out at room temperature.

Scheme I



a

An intramolecular Schmidt reaction of the type shown in eq 1 would constitute an attractive entry into ring systems sporting a nitrogen atom at one of the ring fusion positions. Such ring systems are prominent substructures in a wide variety of alkaloid families.[7] We report that *the intramolecular reaction of alkyl azides with ketones can be accomplished in high yield under remarkably mild and straightforward reaction conditions.*


(1)

The reaction of alkyl azide **5b**[8] is representative of the examples collected in Table I (entry 10). Gas evolution was immediately observed upon dissolution of **5b** in trifluoroacetic acid (TFA).[9]

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(1) (a) Wolff, H. *Org. React.* (*N.Y.*) **1946**, *3*, 307–336. (b) Smith, P. A. S. In *Molecular Rearrangements*; de Mayo, P., Ed.; John Wiley and Sons: New York, 1963; Vol. 1, pp 457–591. (c) Uyeo, S. *Pure Appl. Chem.* **1963**, *7*, 269–283. (d) Abramovich, R. A.; Kyba, E. P. In *The Chemistry of the Azido Group*; Patai, S., Ed.; John Wiley and Sons: London, 1971; pp 221–329. (e) Banthorpe, D. V. In *The Chemistry of the Azido Group*; Patai, S., Ed.; John Wiley and Sons: London, 1971; pp 397–440. (f) Kyba, E. P. In *Azides and Nitrenes: Reactivity and Utility*; Scriven, E. F. V., Ed.; Academic: Orlando, 1984; pp 2–34.

(2) For a list of methods that allow the formal insertion of a primary amine into a carbonyl compound, see: Hoffman, R. V.; Salvador, J. M. *Tetrahedron Lett.* **1989**, *30*, 4207–4210.

(3) (a) Briggs, L. H.; De Ath, G. C.; Ellis, S. R. *J. Chem. Soc.* **1942**, 61–63. (b) Smith, P. A. S. *J. Am. Chem. Soc.* **1948**, *70*, 320–323.

(4) (a) Boyer, J. H.; Hamer, J. *J. Am. Chem. Soc.* **1955**, *77*, 951–954. (b) Boyer, J. H.; Canter, F. C.; Hamer, J.; Putney, R. K. *J. Am. Chem. Soc.* **1956**, *78*, 325–327. (c) Boyer, J. H.; Morgan, L. R., Jr. *J. Am. Chem. Soc.* **1958**, *80*, 2020–2021. (d) Boyer, J. H.; Morgan, L. R., Jr. *J. Am. Chem. Soc.* **1959**, *81*, 3369–3372. (e) Boyer, J. H.; Morgan, L. R., Jr. *J. Org. Chem.* **1959**, *24*, 561–562.

(5) The "intramolecular Schmidt reactions" described by Boyer do not involve a C → N migration per se, but probably involve the elimination of a proton and N_2.[4a,b] Hydride migrations were observed in the reactions of certain aryl aldehydes and alkyl azides, but yields were low, and the scope of the reaction was severely limited.[4c] To our knowledge, the successful insertion of an alkyl azide into a ketone has never been accomplished.

(6) (a) Schultz, A. G.; Ravichandran, R. *J. Org. Chem.* **1980**, *45*, 5008–5009. (b) Schultz, A. G.; McMahon, W. G. *J. Org. Chem.* **1984**, *49*, 1676–1678.

(7) Some recent reviews have appeared. (a) Indolizidine and quinolizidine alkaloids: Herbert, R. B. In *Alkaloids: Chemical and Biological Perspectives*; Pelletier, S. W., Ed.; John Wiley and Sons: New York, 1985; Vol. 3, pp 241–273. (b) Elbein, A. D.; Molyneux, R. J. In *Alkaloids: Chemical and Biological Perspectives*; Pelletier, S. W., Ed.; John Wiley and Sons: New York, 1987; Vol. 5, pp 1–54. (c) Phenanthroindolizidine alkaloids: Gellert, E. In *Alkaloids: Chemical and Biological Perspectives*; Pelletier, S. W., Ed.; John Wiley and Sons: New York, 1987; Vol. 5, pp 55–131. (d) Cephalotaxine alkaloids: Hudlicky, T.; Kwart, L. D.; Reed, J. W. In *Alkaloids: Chemical and Historical Perspectives*; Pelletier, S. W., Ed.; John Wiley and Sons: New York, 1987; Vol. 5, pp 639–690. (e) Pyrrolizidine alkaloids: Robins, D. J. *Adv. Heterocycl. Chem.* **1979**, *24*, 247–291.

(8) The azido ketones were prepared using standard chemistry; details will be provided in the full account of this work.

(9) For the use of trichloroacetic acid in the Schmidt reaction: (a) Reference 3b. (b) Fikes, L. E.; Shechter, H. *Tetrahedron Lett.* **1976**, 2525–2528.