in very small shifts in the position of the Soret band of **4** (although addition of stronger ligands such as imidazole resulted in a significant red shift of the Soret (data not shown), demonstrating the availability of an open coordination site in **4**). Nonetheless, the NMR experiment qualitatively supports the conclusion that various alkenes might differentially inhibit attack of **4** by EDA by occupying a coordination site, thus leading to the modestly different rates of cyclopropanation observed in catalytic reactions.

Summary. The nature of the active catalyst in the rhodium porphyrin-mediated cyclopropanation of alkenes by EDA has been probed. The iodoalkylrhodium complex **4**, presumably produced by attack of iodide on the active metallocarbene, is formed rapidly in situ and is the predominant catalyst over the course of the reaction. Quenching of the carbene with iodide is surprisingly competitive with carbene transfer to the alkene even in the presence of a 25 000-fold excess of the alkene (100 cyclopropanation events for every iodination). Porphyrin **4** is shown to bind alkenes in a reversible fashion. Thus, competition between the alkene and EDA for the vacant coordination site provides a plausible explanation for the observation that different alkenes are cyclopropanated at different rates, even though carbene formation is rate-limiting. A similar scenario has been postulated by Salmeron and Kochi for copper triflate-catalyzed cyclopropanation reactions.[11] Our current model for the catalytic cycle is shown in Figure 6.

These findings may have some practical impact in the design of asymmetric or shape-selective porphyrin cyclopropanation catalysts. For example, it should be possible to use a bulky alkyl ligand to block the most sterically accessible face of a catalyst in which both sides are not equivalent. All subsequent cyclopropanation chemistry would then occur on the modified face of the porphyrin.

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Synthesis and Reactivity Patterns of New Proazaphosphatranes and Quasi-azaphosphatranes $ZP(MeNCH_2CH_2)_3N$

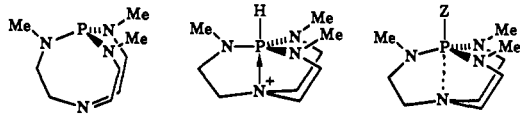
Jian-Sheng Tang and John G. Verkade*

Contribution from Gilman Hall, Department of Chemistry, Iowa State University, Ames, Iowa 50011. *Received September 21, 1992*

Abstract: Partial bridgehead–bridgehead P←N transannulation in $S_2CP(MeNCH_2CH_2)_3N$ (**4**) stabilizes this unusual CS_2 adduct, facilitating the synthesis of a series of $RS(S)CP(MeNCH_2CH_2)_3N^+$ cations from the reaction of **4** with RX (**5**, R = Me; **6**, R = CH_2=$CHCH_2$; **7**, R = Et; **8**, R = *n*-Pr; **9**, R = *n*-Bu; **10**, R = *i*-Pr). The relative rates of formation of **5–10** are in accord with S_N2 attack of sulfur on the α carbon of RX. The structure determination of **5**(I) by X-ray means revealed that formation of cation **5** from **4** is accompanied by shortening of the transannular interaction from 3.008 to 2.771 Å. We also report the synthesis of a series of regioisomeric products of the reaction of $S{=}P(MeNCH_2CH_2)_3N$ (**11**) with RX, namely, $RSP(MeNCH_2CH_2)_3N^+$ (R = Me, Et, *n*-Bu) and $S{=}P(MeNCH_2CH_2)_3NR^+$ (R = Me, Et). The slow decomposition of **4** to **11** in solution is also described.

Introduction

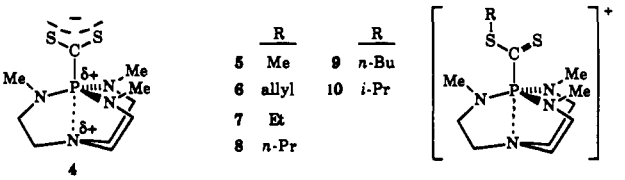
The bicyclic proazaphosphatrane **1** has been shown to be a remarkably strong base, reacting with a proton to give the stable azaphosphatrane **2**.[1-3] Cation **2** features a transannular P←N



1 2 3

covalent bond that forms via inversion of the bridgehead nitrogen.[1-3] We have also recently demonstrated that **1** forms quasi-azaphosphatranes **3**, in which the $P{-}N_{ax}$ bond distance is intermediate between the sum of the P and N van der Waals radii (3.35 Å) and the covalent transannular bond distance in **2**, depending on the nature of Z.[4]

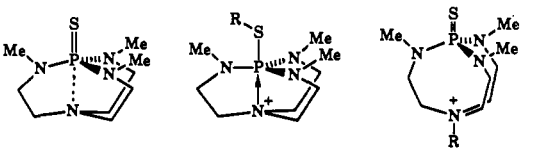
As part of our continuing exploration of the chemical consequence of partial transannulation in these systems, we report herein the synthesis of a series of quasi-azaphosphatrane cations **5–10**



4

	R		R
5	Me	9	*n*-Bu
6	allyl	10	*i*-Pr
7	Et		
8	*n*-Pr		

and rationalize the relative rates with which these products are formed from **4**[4] and the RX reagents. We also report that the proazaphosphatrane **11** described earlier[2,5] reacts with MeI to give



11 12a, R = Me; 13a, R = Et; 14a, R = *n*-Bu 12b, R = Me; 13b, R = Et

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the regioisomers **12a**(I) and **12b**(I) whereas **4** in the presence of MeI forms only **5**(I). The crystal structure of **5**(I) was communicated earlier.[4] Although the analogous regioisomers are formed from **11** in the presence of EtI (i.e., **13a,b**), only **14a** is realized with *n*-BuI, and no reaction is observed using *i*-PrI. The decomposition of **4** to **11** is also described.

Discussion

Synthesis and Reactions. Although we reported the synthesis of adduct **4** earlier,[4] its stability relative to rearrangement 1, characteristic of the acyclic analogues, is worthy of comment.

$$\underset{\mathbf{15}}{(R_2N)_3\overset{+}{P}C(S)S^-} \longrightarrow \underset{\mathbf{16}}{(R_2N)_2PS(S)CNR_2} \qquad (1)$$

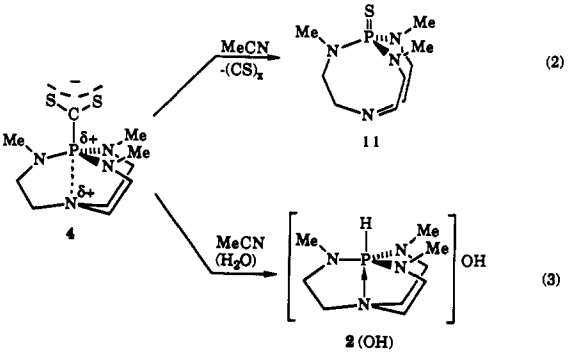
Thus $(R_2N)_3P$ in the presence of CS_2 provides spectroscopic evidence for **15** at −20 °C, but this zwitterion rapidly rearranges at room temperature to give **16**.[6] In the presence of additional CS_2, up to two more dithiocarbamate linkages can be formed.[7] The relative stability of **4** is attributed to increased stability of the P→C donor bond by partial transannular N→P bonding which shortens the latter distance by 10.2% from the sum of the P and N van der Waals radii (3.35 Å)[8] to 3.008 Å.[2] Transannular bonding permits delocalization of the N_{ax} lone pair and the P←C bond pair over a three-center four-electron MO system that also delocalizes the positive charge as shown in **4**. The stabilization of adduct **4** by the enhanced basicity of phosphorus is consistent with the known stability of $(n\text{-Bu})_3P^+C(S)S^-$, for example,[9] and this stability facilitates the synthesis of the alkylated derivatives **5**–**10**.

The red solids **5**(I) and **6**(I) are formed rapidly (<5 min) and quantitatively (**5**(I) with some exothermicity) by adding MeI and CH_2=$CHCH_2I$, respectively, to **4** at room temperature. Although high-resolution EI mass spectroscopy failed to detect a parent cation for **5**(I), low-resolution FAB spectra revealed peaks for the parent cations of both **5**(I) and **6**(I), and curiously an M_2I^+ peak for **5**(I) for reasons that are not clear.

Addition of EtI to **4** failed to produce even a color change after 3 min. Adding MeCN to dissolve **4** caused the solution to turn violet after 5 min of stirring at room temperature. Monitoring by ^{31}P NMR spectroscopy, however, revealed that 20 min was required to complete the reaction. Evaporation of the volatiles under vacuum gave pure **7**(I) in quantitative yield. As in the case of **5**(I), the FAB mass spectrum of **7**(I) featured M^+ and M_2I^+ peaks. Analogous reactions of *n*-PrI, *n*-BuI, and *i*-PrI with **4** in MeCN at room temperature required 35 min, 55 min, and >6 h, respectively, for quantitative formation (as monitored by ^{31}P NMR spectroscopy) of **8**(I), **9**(I), and **10**(I). The relative reaction rates in MeCN of RX with **4**, namely, MeI ≅ CH_2=$CHCH_2I$ > EtI > *n*-PrI ≫ *i*-PrI, are consistent with S_N2 attack by the negatively charged sulfur in **4** on the α carbon of RX. This conclusion is supported by the relative reaction rates of *n*-PrI and *n*-PrBr (35 min and >6 h, respectively) with **4** to give **8**(I) and **8**(Br), and the failure of compounds possessing still poorer leaving halides such as CD_2Cl_2, $CDCl_3$, $ClCO_2Et$, $ClSiMe_3$, PhC(O)Cl, and $CF_3CO_2SiMe_3$ to react with **4** in MeCN.

Both **5**(I) and **11** could conceivably undergo alkylation of the bridgehead nitrogen with MeI. Whereas this reaction in MeCN was not realized in the case of **5**(I), **11** gave rise to regioisomers in which the sulfur atom was alkylated (**12a**) as well as the bridgehead nitrogen (**12b**) in a 1.4:1.0 ratio, as monitored by ^{31}P NMR spectroscopy. Compound **11** in the presence of EtI formed **13a** and **13b** (8.2:1) whereas with *n*-BuI only **14a** was detected. With *i*-PrI, no reaction was indicated by ^{31}P NMR spectroscopy. These results accord with the ideas that (a) the bridgehead nitrogen in **5** is less nucleophilic than that in **11** (a point we justify on structural grounds later) and (b) the bridgehead nitrogen in **11** is more sensitive to the bulk of the alkylating group than the sulfur. That the ratios of the regioisomers formed are kinetically rather than thermodynamically established was shown by isolating them in the case of **12a** and **12b** and demonstrating that neither interconverted to the other upon heating in MeCN at 40–45 °C for 10 h.

As stated earlier, **4** is very stable with respect to the rearrangement observed for acyclic analogues (reaction 1). Indeed **4** is stable for months in the solid state in an inert atmosphere. Over a period of weeks in MeCN solution at room temperature, however, monitoring by ^{31}P NMR spectroscopy showed that **4** decomposes to **11**, varying amounts of **2**(OH) (depending upon



(2)

(3)

the moisture content of the solvent), and presumably $(CS)_x$. Reactions 2 and 3 are accelerated to completion in about 30 min in boiling MeCN. The proportion of the ^{31}P NMR peaks for **11** and **2**(OH) ranged from 3:1 for CD_3CN dried only with molecular sieves to 20:1 for CD_3CN dried with molecular sieves followed by refluxing over and distillation from CaH_2. It is plausible to suggest that the equilibrium (reaction 4) observed for acyclic

$$(R_2N)_3\overset{+}{P}C(S)S^- \rightleftharpoons (R_2N)_3P + CS_2 \qquad (4)$$

analogues[6] of **4** lies further to the left in the case of **4**, owing to the greater basicity of phosphorus in **4**, as suggested earlier. However, to the extent that **4** does dissociate to CS_2 and **1**, protonation and sulfuration of the latter compound to **2** and **11**, respectively, are apparently competing processes in reaction 2. The sulfuration of **1** by CS_2 in reaction 2 is related to reaction 5, which was reported earlier.[10]

$$Et_3P + RN{=}C{=}S \rightarrow Et_3P{=}S + RN{\equiv}C \qquad (5)$$

By contrast, the quasi-azaphosphatrane cations **5**–**10** are very stable in solution as well as in the solid state. Thus **5**(I) is stable at room temperature in the solid state for at least 8 months or in moist MeCN for at least 2 months. Even heating the solution at 45 °C for 10 h produced no changes detectable by ^{31}P NMR spectroscopy.

Structural Considerations. The ORTEP drawing of **5**(I) in Figure 1 features a P–N_{ax} distance of 2.771 Å (which is 17% shorter than the sum of the P and N van der Waals radii) and an upwardly protruding N_{ax} atom suggestive of partial transannulation. The N_{eq}–P–N_{eq} angles (av 113.4°) are substantially larger than those (av 105°) in *trans*-$Cl_2Pt(\mathbf{1})_2$,[2] in which transannulation is absent (P–N_{ax} = 3.33 Å). This angle difference also reflects the existence of partial transannulation in **5**(I). Of the three quasi-azaphosphatrane structures known (i.e., **4**, **5**(I) and **11**), that of **5**(I) is closest to adopting the trigonal bipyramidal stereochemistry of **2**. Interestingly, the shortening of the P–N_{ax} distance from 3.008 Å in **4**[2] to 2.771 Å in **5**(I) does not result in an upfield ^{31}P chemical shift, as is usually associated with an increase in phosphorus coordination in phosphatranes.[1,3,4,11-13]

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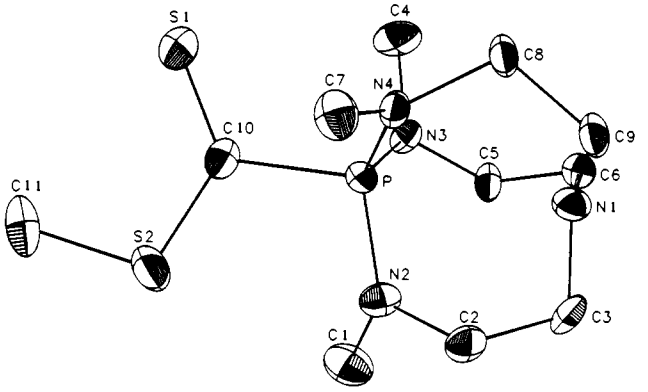


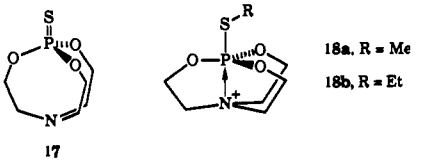
Figure 1. ORTEP drawing of 5(I). Thermal ellipsoids are at the 50% probability level.

Indeed $\delta(^{31}P)$ moves somewhat to lower field, progressing from 21.8 ppm in **4** to 24.1 ppm in **5** and remaining near this value for **6–10** (see Experimental Section). It would be expected that if the degree of transannulation observed from structural metrics in the solid state remained approximately constant upon dissolution, that the ^{31}P NMR chemical shift would also not change substantially. Earlier we reported a solution $\delta(^{31}P)$ value of 21.3 ppm for **4**,[5] whose P–N_{ax} distance (3.008 Å) is 10% shorter than the sum of the van der Waals radii (3.34 Å) and whose N_{eq}–P–N_{eq} bond angle of 110.3° is ~6° larger than in that *trans*-(**4**)$_2$PtCl$_2$, for which the corresponding metrics are 3.33 Å and 104.5°.[2] The solution $\delta(^{31}P)$ value for **4** is very closely matched by its solid-state counterpart (21.63 ppm[14]). This is also true for **7**(I), whose $\delta(^{31}P)$ solution value of 23.62 ppm (see Experimental Section) is closely matched by its solid-state chemical shift of 23.22 ppm.[14] Since even small bond angle changes around phosphorus are well-known to severely affect ^{31}P chemical shifts,[15] we conclude that, at least for quasi-azaphosphatranes, the solution and solid-state structures are closely identical. Phosphorus-31 coupling to the N(CH$_2$)$_3$ protons and carbons has been observed in fully transannulated cations such as **2**.[1,11] However, in none of the compounds **4–14** are such couplings observed, therefore precluding the nondetection of this coupling as a criterion for the total absence of transannulation.

The greater stability in solution of **5**(I) relative to **4** is rationalized on the basis of the overall positive charge on cation **5**, which would tend to strengthen its bonds. The greater hydrolytic stability of **5** (compared with **4**) may arise from the greater delocalization of the positive charge of **5** in the axial bonding system, which would render the phosphorus and its ligated carbon less electrophilic.

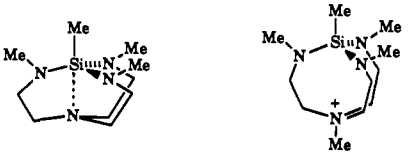
It should be noted that the decrease in the P–N_{ax} distance from **11** (3.25 Å)[2] to **4** (3.008 Å)[2] to **5** (2.771 Å) with concomitant opening of the N_{eq}–P–N_{eq} bond angles (106.8°, 110.3°, and 113.4°, respectively) is not determined by the bulk of the exocyclic phosphorus substituent. Because the size of this group actually increases from S to CS$_2$ to SCSMe$^+$ in this series (i.e., **11** to **4** to **5**), it is clear that increasing electron withdrawing effects prevail.

Binding an alkyl cation to a sulfur of **4** clearly enhances the polarization of the P lone pair toward the C. The shorter P←N_{ax} distance in cation **5** and its higher positive charge compared with that of **11** also renders the bridgehead nitrogen of cation **5** less nucleophilic toward RX. Whether the regioisomers **12a**, **13a**, and **14a**, derived from alkylation of the sulfur of **11**, possess the azaphosphatrane structure as shown (i.e., containing a normal five-coordinate phosphorus) is not certain in the current absence of suitable crystals for X-ray analysis. While the upfield ^{31}P chemical shift from **11** to the cations **12a**, **13a**, and **14a** is substantial (ca. 25 ppm), it is not as strong as that observed earlier in going from **17** to the cations **18a** and **18b** (ca. 55 ppm).[16] The



17

fully transannulated structure for **18b** was confirmed earlier by X-ray means.[17] Alkylation of the bridgehead nitrogen of **11** to give the regioisomers **12b** and **13b** leads to only a very small change (ca. 0.2 ppm) in the ^{31}P chemical shift. This suggests that any stereoelectronic changes in the phosphorus environment caused by conversion of the nearly planar nitrogen in **11**[2] to a presumably nearly tetrahedral geometry are not registered in the ^{31}P chemical shift. By contrast, the ^{29}Si chemical shift in **19** moves 15.3 ppm



19 20

downfield upon quaternization of the bridgehead nitrogen to give **20**.[18] The increased sensitivity of the ^{29}Si chemical shift to the stereochemical change induced by quaternization can be attributed in part to the fact that the transannular distance in **19** is 24% shorter than the sum of the van der Waals radii[2] while in **11** it is only 3% shorter.[2]

Experimental Section

All procedures were carried out in an atmosphere of argon using solvents dried by standard means. NMR spectrometers employed were a Nicolet NT-300 or a Varian VXR-300 for ^1H spectra (except in the case of **5**(I), for which a Unity-500 was used), a Bruker WM-200 for ^{31}P spectra, and a Varian VXR-300 for ^{13}C spectra. Standards for the NMR spectra were TMS (^1H, internal), 85% H_3PO_4 (^{31}P, external), and the δ 118.20 peak of the solvent CD_3CN (^{13}C, internal). Infrared spectra were recorded with a Bruker IFS-113 V spectrometer. Fast atom bombardment spectra were recorded with a KRATOS MS-50 spectrometer using MeCN as the solvent for **5–10**, **12a**, **13a,b**, and **14a**, and DMSO for **12b**. The matrix employed was 3-nitrobenzyl alcohol in all cases except for **12b**, for which thioglycerol was used. Elemental analyses were performed by Galbraith Laboratories, Inc. X-ray data collection and the structure solution were carried out at the Iowa State Molecular Structure Laboratory. Refinement calculations were performed on a Digital Equipment Corp. Micro VAX II computer using the CAD4-SDP programs. Starting material **4** was prepared by our previously published method.[1,5]

[CH$_3$SC(S)P(NMeCH$_2$CH$_2$)$_3$N]I (5(I)). MeI (1.88 g, 13.2 mmol) was syringed into a 10-mL flask containing 0.12 g (0.41 mmol) of brown solid **4**. An exothermic reaction was observed, and a red solid was formed immediately. Acetonitrile was added to the reaction mixture until all of the red solid was dissolved. The red solution was stirred for 1–2 min, and the volatiles were removed in vacuo to afford spectroscopically pure red solid **5**(I) (0.178 g, quantitative) according to its ^{31}P, ^1H, and ^{13}C NMR spectra. The red solid (0.178 g) was redissolved in 3 mL of dry acetonitrile. The solution was cooled in a freezer (about −25 °C) overnight to grow large crystals. The red solution was removed carefully with a syringe, and the crystals were dried in vacuo giving 0.079 g of crystals suitable for X-ray analysis. ^{31}P NMR (CD_3CN): δ 24.10. ^1H NMR (CD_3CN): δ 2.72 (s, 3 H, SCH_3), 2.85 (t, 6 H, $N_{ax}CH_2$, $^3J_{HH}$ = 5.7 Hz), 2.86 (d, 9 H, $N_{eq}CH_3$, $^3J_{PH}$ = 11.1 Hz), 3.01 (td, 6 H, $N_{eq}CH_2$, $^3J_{PH}$ = 15.6 Hz, $^3J_{HH}$ = 5.7 Hz). ^{13}C NMR (CD_3CN): δ 21.25 (d, SCH_3, $^3J_{PC}$ = 0.1 Hz), 38.08 (d, $N_{eq}CH_3$, $^2J_{PC}$ = 2.0 Hz), 50.39 (d, $N_{eq}CH_2$, $^2J_{PC}$ = 3.5 Hz), 51.77 ($N_{ax}C$), 232.50 (d, PC, $^1J_{PC}$ = 154.9 Hz). IR (KBr pellet): 640(s), 887(s), 1009(s), 1041(s), 1074(s), 1101(s), 1203(s), 1222.5(s), 1323(s), 1381(s), 1405(s), 1460(s), 2856(m), 2951(m). MS (FAB) *m/z*: 307.1 (100, [MeSC(S)P(NMeCH$_2$CH$_2$)$_3$N]$^+$), 741.2 (1.0, [(MeSC(S)P(NMeCH$_2$CH$_2$)$_3$N)$_2$I]$^+$). Anal. Calcd. for C$_{11}$H$_{24}$IN$_4$PS$_2$:

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C, 30.43; H, 5.58; N, 12.91. Found: C, 30.45; H, 5.26; N, 12.72.

[CH$_2$=CHCH$_2$SC(S)P(NMeCH$_2$CH$_2$)$_3$N]I (6(I)). Excess allyl iodide (0.5 mL) was placed in a 5-mL flask containing 0.050 g (0.17 mmol) of **4** and 3 mL of CD_3CN. A red solution was formed immediately after stirring for 5 min, and the volatiles were removed in vacuo to give a quantitative yield of product (0.078 g). ^{31}P NMR (CD_3CN): δ 23.50. ^{1}H NMR (CD_3CN): δ 2.84 (t, 6 H, $N_{ax}CH_2$, $^3J_{HH}$ = 5.7 Hz), 2.86 (d, 9 H, $N_{eq}CH_3$, $^3J_{PH}$ = 11.1 Hz), 3.01 (td, 6 H, $N_{eq}CH_2$, $^3J_{PH}$ = 15.6 Hz, $^3J_{HH}$ = 5.4 Hz), 3.98 (d, 2 H, SCH_2, $^3J_{HH}$ = 6.9 Hz), 5.25 (dd, 1 H, H_b of $-CH_c=CH_aH_b$, $^2J_{H_aH_b}$ = 1.2 Hz, $^3J_{H_bH_c}$ (cis) = 10.8 Hz), 5.40 (dd, 1 H, H_a, $^2J_{H_aH_b}$ = 1.2 Hz, $^3J_{H_aH_c}$ (trans) = 17.4 Hz), 5.88 (m, 1 H, H_c). ^{13}C NMR (CD_3CN): δ 38.29 (d, $N_{eq}CH_3$, $^2J_{PC}$ = 1.4 Hz), 40.22 (d, SC, $^3J_{PC}$ = 1.4 Hz), 50.49 (d, $N_{eq}CH_2$, $^2J_{PC}$ = 3.7 Hz), 51.82 ($N_{ax}C$), 121.75, 130.30, 231.07 (d, PC, $^1J_{PC}$ = 153.2 Hz). MS (FAB) *m/z*: 333.1 (100, [CH$_2$=CHSC(S)P(NMeCH$_2$CH$_2$)$_3$N]$^+$).

[EtSC(S)P(NMeCH$_2$CH$_2$)$_3$N]I (7(I)). EtI (1.35 g, 8.6 mmol) was syringed into a 10-mL flask containing 0.080 g (0.27 mmol) of brown solid **4**. No heat evolution or color change was observed within 3 min. Acetonitrile (8 mL) was added with a syringe, and after stirring for 5 min, a violet solution was formed, although the ^{31}P NMR spectrum showed that the reaction was incomplete. After the solution was stirred for another 14 min, the reaction was complete and the volatiles were removed in vacuo to give a quantitative yield (0.12 g) of NMR spectroscopically pure orange solid **7(I)**. ^{31}P NMR (CD_3CN): δ 23.62. ^{1}H NMR (CD_3CN): 1.32 (t, 3 H, $^3J_{HH}$ = 7.8 Hz), 2.82 (t, 6 H, $N_{ax}CH_2$, $^3J_{HH}$ = 5.7 Hz), 2.86 (d, 9 H, $N_{ax}CH_3$, $^3J_{PH}$ = 10.8 Hz), 2.99 (td, 6 H, $N_{eq}CH_2$, $^3J_{PH}$ = 15.6 Hz, $^3J_{HH}$ = 5.7 Hz), 3.31 (q, 2 H, SCH_2, $^3J_{HH}$ = 7.8 Hz). ^{13}C NMR (CD_3CN) 11.27 (SC*C*), 32.15 (d, SC, $^3J_{PC}$ = 1.1 Hz), 38.10 ($N_{eq}CH_3$, $^2J_{PC}$ = 1.9 Hz), 50.38 (d, $N_{eq}CH_2$, $^2J_{PC}$ = 3.4 Hz), 51.79 ($N_{ax}C$). MS (FAB) *m/z*: 321.1 (100, [EtSC(S)P(NMeCH$_2$CH$_2$)$_3$N]$^+$).

[*n*-PrSC(S)P(NMeCH$_2$CH$_2$)$_3$N]I (8(I)). *n*-PrI (1.19 g, 7.0 mmol) was added via syringe to **4** (0.10 g, 0.34 mmol). No color change was observed in 8 min, and so 10 mL of acetonitrile was added. The mixture was stirred for 1.5 h and evaporated in vacuo to give a quantitative yield (0.157 g) of NMR spectroscopically pure red solid **8**. ^{31}P NMR (CD_3CN): δ 23.82. ^{1}H NMR (CD_3CN): 1.02 (t, 3 H, $SCCCH_3$, $^3J_{HH}$ = 7.2 Hz), 1.73 (m, 2 H, $SCCH_2$), 2.83 (t, 6 H, $N_{ax}CH_2$, $^3J_{HH}$ = 5.7 Hz), 2.86 (d, 9 H, $N_{eq}CH_3$, $^3J_{PH}$ = 11.1 Hz), 3.00 (td, 6 H, $N_{eq}CH_2$, $^3J_{PH}$ = 15.6 Hz, $^3J_{HH}$ = 5.7 Hz), 3.31 (t, 2 H, SCH_2, $^3J_{HH}$ = 7.5 Hz). ^{13}C NMR (CD_3CN): δ 13.76 (SCC*C*), 20.48 (SC*C*), 39.43 (SC), 38.03 (d, $N_{eq}CH_3$, $^2J_{PC}$ = 1.8 Hz), 50.37 (d, $N_{eq}CH_2$, $^2J_{PC}$ = 3.2 Hz), 51.82 ($N_{ax}CH_2$), 231.68 (d, PC, $^1J_{PC}$ = 153.7 Hz). MS (FAB) *m/z* 335.0 (100, [*n*-PrSC(S)P(NMeCH$_2$CH$_2$)$_3$N]$^+$), 796.9 (0.4, [(*n*-PrSC(S)P(NMeCH$_2$CH$_2$)$_3$N)$_2$I]$^+$).

[*n*-BuSC(S)P(NMeCH$_2$CH$_2$)$_3$N]I (9(I)). Excess *n*-butyl iodide (0.5 mL) was placed in an NMR tube containing 0.018 g (0.061 mmol) of **4** and 0.5 mL of CD_3CN. After 15 min of shaking, the ^{31}P NMR spectrum of the pink solution showed a new peak at 24.4 ppm of ~0.1 the intensity of that of the starting material. After standing overnight, the pink solution was evaporated under vacuum to give a quantitative yield (0.028 g) of NMR spectroscopically pure red solid **9(I)**. ^{31}P NMR (CD_3CN): δ 24.04. ^{1}H NMR (CD_3CN): δ 0.93 (t, 3 H, $SCCCCH_3$, $^3J_{HH}$ = 7.5 Hz), 1.73 (m, 2 H, $SCCCH_2$), 1.68 (m, 2 H, $SCCH_2$), 2.83 (t, 6 H, $N_{ax}CH_2$, $^3J_{HH}$ = 5.7 Hz), 2.86 (d, 9 H, $N_{eq}CH_3$, $^3J_{PH}$ = 10.8 Hz), 2.99 (td, 6 H, $N_{eq}CH_2$, $^3J_{PH}$ = 15.6 Hz, $^3J_{HH}$ = 5.7 Hz), 3.33 (t, 2 H, SCH_2, $^3J_{HH}$ = 7.5 Hz). ^{13}C NMR (CD_3CN): δ 13.38 (SCCCC), 22.49 (SCC*C*), 28.44 (SC*C*), 37.01 (d, SC, $^3J_{PC}$ = 0.9 Hz), 37.69 (d, $N_{ax}CH_3$, $^2J_{PC}$ = 1.8 Hz), 49.98 (d, $N_{eq}CH_2$, $^2J_{PC}$ = 3.2 Hz), 51.44 ($N_{ax}C$), 231.05 (d, PC, $^1J_{PC}$ = 154.1 Hz). MS (FAB) *m/z* 349.1 (100, [*n*-BuSC(S)P(NMeCH$_2$CH$_2$)$_3$N]$^+$), 825.1 (0.3, [(*n*-BuSC(S)P(NMeCH$_2$CH$_2$)$_3$N)$_2$I]$^+$).

[*i*-PrSC(S)P(NMeCH$_2$CH$_2$)$_3$N]I (10(I)). *i*-PrI (0.31 g, 1.8 mmol) was added to an NMR tube containing 0.020 g (0.092 mmol) of **4** and 0.8 mL of MeCN. After 5 h, ^{31}P NMR spectroscopy revealed an incomplete reaction. The mixture was allowed to stand for an additional 43 h, at which point the ^{31}P NMR spectrum showed that the reaction was complete. The solvent was removed in vacuo to give a quantitative yield (0.031 g) of NMR spectroscopically pure blue-violet solid **10**. ^{31}P NMR (CD_3CN): δ 23.82. ^{1}H NMR (CD_3CN): δ 1.39 (d, 6 H, $SCCH_3$, $^3J_{HH}$ = 6.9 Hz), 2.82 (t, 6 H, $N_{ax}CH_2$, $^3J_{HH}$ = 5.7 Hz), 2.86 (d, 9 H, $N_{eq}CH_3$, $^3J_{PH}$ = 11.1 Hz), 2.99 (td, 6 H, $N_{eq}CH_2$, $^3J_{PH}$ = 15.6 Hz, $^3J_{HH}$ = 5.7 Hz), 4.06 (septet, 1 H, SCH, $^3J_{HH}$ = 6.9 Hz). ^{13}C NMR (CD_3CN): δ 20.53 (SC*C*), 38.11 (d, $N_{ax}CH_3$, $^2J_{PC}$ = 1.7 Hz), 42.45 (d, SC, $^3J_{PC}$ = 0.9 Hz), 50.39 (d, $N_{eq}CCH_2$, $^2J_{PC}$ = 2.9 Hz), 51.87 ($N_{ax}C$), 231.67 (d, PC, $^1J_{PC}$ = 154.2 Hz). MS (FAB) *m/z* 335.0 (100, [*i*-PrSC(S)P(NMeCH$_2$CH$_2$)$_3$N]$^+$), 796.9 (0.2, [(*i*-PrSC(S)P(NMeCH$_2$CH$_2$)$_3$N)$_2$I]$^+$).

[*n*-PrSC(S)P(NMeCH$_2$CH$_2$)$_3$N]Br (8(Br)). Excess *n*-PrI (0.70 g, 4.1 mmol) was added to an NMR tube containing 0.0375 g (0.128 mmol) of **4**. No heat evolution or color change could be observed in 8 min. At this point 0.5 mL of CD_3CN was added and the mixture was shaken for 0.5 h. The ^{31}P NMR spectrum showed a new peak at 24.22 ppm with ~5% of the intensity of the starting compound. Upon standing overnight, the mixture gave a violet solution with a single peak at 24.22 ppm in the ^{31}P NMR spectrum. The volatiles were removed in vacuo to afford a quantitative yield (0.059 g) of NMR spectroscopically pure pink solid **8(Br)**. ^{31}P NMR (CD_3CN): δ 24.22. ^{1}H NMR (CD_3CN): δ 1.02 (t, 3 H, $SCCCH_2$, $^3J_{HH}$ = 7.5 Hz), 1.73 (m, 2 H, $SCCH_2$), 2.83 (t, 6 H, $N_{ax}CH_2$, $^3J_{HH}$ = 5.7 Hz), 2.86 (d, $N_{eq}CH_3$, $^3J_{PH}$ = 11.1 Hz), 3.00 (td, 6 H, $^3J_{PH}$ = 15.6 Hz, $^3J_{HH}$ = 5.7 Hz), 3.30 (t, 2 H, SCH_2, $^3J_{HH}$ = 7.5 Hz). ^{13}C NMR (CD_3CN): δ 13.75 (SCC*C*), 20.49 (SC*C*), 38.04 ($N_{eq}CH_3$, $^2J_{PC}$ = 1.8 Hz), 39.42 (SC), 50.36 (d, $N_{eq}CH_2$, $^2J_{PC}$ = 3.2 Hz), 51.81 ($N_{ax}C$), 231.68 (d, PC, $^1J_{PC}$ = 153.16 Hz. MS (FAB) *m/z*: 335.0 (100, [*n*-PrSC(S)P(NMeCH$_2$CH$_2$)$_3$N]$^+$), 756.0 (0.5, [(*n*-PrSC(S)P(NMeCH$_2$CH$_2$)$_3$N)$_2$Br]$^+$).

Reaction of 11 with MeI. Excess MeI (0.50 mL) was added to a solution of **11** (0.048 g, 0.19 mmol) in acetonitrile (5 mL). The solution was stirred at 40 °C for 10 h, after which the solvent was removed in vacuo to give a quantitative yield of a white solid. ^{31}P NMR spectroscopy in DMSO showed two signals (49.42 and 75.77 ppm, respectively) in the ratio of 1.4:1.0. The white solid was stirred with 5 mL of acetonitrile for 3 h, filtered in vacuo, and washed with 4 mL of acetonitrile to give 0.03 g (40%) of white solid compound **12b** according to its ^{31}P and ^{1}H NMR spectra. ^{31}P NMR (DMSO-d_6): δ 75.97. ^{1}H NMR (DMSO-d_6): δ 2.70 (d, 9 H, $N_{eq}CH_3$, $^3J_{PH}$ = 9.3 Hz), 3.12 (s, 3 H, $N_{ax}CH_3$), 3.19 (m, 6 H, $N_{ax}CH_2$), 3.85 (m, $N_{eq}CH_2$). The filtrate was evaporated in vacuo to give 0.038 g (51%) of white solid **12a** according to its ^{31}P, ^{1}H, and ^{13}C NMR spectra. ^{31}P NMR (DMSO-d_6): δ 49.42. ^{1}H NMR (DMSO-d_6): δ 2.42 (d, 3 H, SCH_3, $^3J_{PH}$ = 13.5 Hz), 2.78 (t, 6 H, $N_{ax}CH_2$, $^3J_{HH}$ = 5.4 Hz), 2.82 (d, $N_{eq}CH_3$, 9 H, $^3J_{PH}$ = 12.6 Hz), 3.01 (td, 6 H, $N_{eq}CH_2$, $^3J_{PH}$ = 15.6 Hz, $^3J_{HH}$ = 5.4 Hz). ^{13}C NMR (CD_3CN): δ 15.20 (d, SC, $^2J_{PC}$ = 5.1 Hz), 36.38 (d, $N_{eq}CCH_3$, $^2J_{PC}$ = 4.6 Hz), 50.57 (d, $N_{eq}CH_2$, $^2J_{PC}$ = 2.8 Hz), 51.38 ($N_{ax}C$). MS (FAB) *m/z* for **12a**: 263.1 (100, [MeS-P(NMeCH$_2$CH$_2$)$_3$N]$^+$), 653.0 (0.2, [(MeS-P(NMeCH$_2$CH$_2$)$_3$N)$_2$I]$^+$). MS (FAB) *m/z* for **12b**: 263.1 (100, [S=P(NMeCH$_2$CH$_2$)$_3$NMe]$^+$), 653.1 (1.3, [(S=P(NMeCH$_2$CH$_2$)$_3$NMe)$_2$I]$^+$).

Compound **12a** (10 mg) in CH_3CN (5 mL) was heated at 40–45 °C for 10 h. The solvent was removed in vacuo to give a white solid whose ^{31}P NMR (DMSO-d_6) spectrum showed a single peak at 49.42 ppm characteristic of **12a**. Similarly 8 mg of **12b** in CH_3CN (5 mL) was heated at 40–45 °C for 10 h. The solvent was removed in vacuo to give a white solid whose ^{31}P NMR (DMSO-d_6) showed a single peak at 75.77 ppm characteristic of **12b**.

Reaction of 11 with EtI. Ethyl iodide (1.0 mL) was added to a solution of **11** (0.051 g, 0.21 mmol) in acetonitrile (7 mL). The solution was heated at 55 °C for 43 h to give a clear solution. The solvent was removed in vacuo to give a quantitative yield (0.090 g) of a white solid mixture of **13a** and **13b**. A ^{31}P NMR spectrum of the mixture in DMSO-d_6 solution showed peaks at 50.42 (**13a**) and 75.91 ppm (**13b**) in the ratio of 8.2:1.0, respectively. Because **13b** was not soluble in acetonitrile, ^{1}H and ^{13}C NMR spectra of the mixture only showed signals for compound **13a**. ^{31}P NMR (DMSO-d_6) for **13a**: δ 50.42. ^{1}H NMR (DMSO-d_6) for **13a**: δ 1.30 (dt, 3 H, $SCCH_3$, $^4J_{PH}$ = 2.7 Hz, $^3J_{HH}$ = 7.5 Hz), 2.75 (t, 6 H, $N_{ax}CH_2$, $^3J_{HH}$ = 5.1 Hz), 2.79 (d, 9 H, $N_{eq}CH_3$, $^3J_{PH}$ = 12.6 Hz), 2.98 (td, partially overlapping with SCH_2 signal, $N_{eq}CH_2$, $^3J_{PH}$ = 14.7 Hz, $^3J_{HH}$ = 5.1 Hz), 2.98 (SCH_2, overlapping with $N_{eq}CH_2$ signal). ^{13}C NMR (CD_3CN) for **13a**: δ 15.82 (d, SC*C*, $^3J_{PC}$ = 6.0 Hz), 27.95 (d, SC, $^2J_{PC}$ = 5.0 Hz), 36.36 (d, $N_{eq}CCH_3$, $^2J_{PC}$ = 4.3 Hz), 50.64 (d, $N_{eq}CH_2$, $^2J_{PC}$ = 2.4 Hz), 51.53 ($N_{ax}C$). However, a ^{1}H NMR spectrum of the mixture in DMSO-d_6 solution clearly showed not only the signals of **13a** but also the characteristic multiplet for the $N_{eq}CH_2$ protons of **13b** (similar to those in **12b**) at 3.56–4.01 ppm. Other peaks of **13b** were not resolved because of low intensity and/or overlap with peaks belonging to **13a**. ^{31}P NMR (DMSO-d_6 for **13b**): δ 75.91. MS (FAB) *m/z* for the mixture: 277 (100, [EtS-P(NMeCH$_2$CH$_2$)$_3$N]$^+$ and [S=P(NMeCH$_2$CH$_2$)$_3$NEt]$^+$), 681.3 (0.4, [(EtS-P(NMeCH$_2$CH$_2$)$_3$N)$_2$I]$^+$ and [(S=P(NMeCH$_2$CH$_2$)$_3$NEt)$_2$]$^+$).

Reaction of 11 with *n*-BuI. To a solution of **11** (0.11 g, 0.45 mmol) in acetonitrile (4 mL) was added 3 mL of *n*-butyl iodide. The solution was stirred at 50–55 °C for 4 days and then evaporated in vacuo to give a quantitative yield (0.19 g) of white solid **14a**. ^{31}P NMR (DMSO-d_6): δ 51.50. ^{1}H NMR (DMSO-d_6): δ 0.88 (t, 3 H, $SCCCCH_3$, $^3J_{HH}$ = 7.4 Hz), 1.39 (m, 2 H, $SCCCH_2$), 1.62 (m, 2 H, $SCCH_2$), 2.74 (t, 6 H, $N_{ax}CH_2$, $^3J_{HH}$ = 5.1 Hz), 2.79 (d, 9 H, $N_{eq}CH_3$, $^3J_{PH}$ = 12.6 Hz), 2.98 (td, 6 H, $N_{eq}CH_2$, $^3J_{PH}$ = 17.1 Hz, $^3J_{HH}$ = 5.1 Hz), ~3.0 (SCH_2, overlapping with $N_{eq}CH_2$). ^{13}C NMR (CD_3CN): δ 13.80 (SCCCC), 22.59 (SCC*C*), 33.19 (SC*C*), 33.33 (d, SC, $^2J_{PC}$ = 3.4 Hz), 36.40 (d, $N_{eq}CH_3$, $^2J_{PC}$ = 5.0 Hz), 50.61 (d, $N_{eq}CH_2$, $^2J_{PC}$ = 2.9 Hz), 51.58

Table I. Selected Bond Distances and Angles in 5(I)

	Bond Distances (Å)		
P-N1	2.771(4)	P-N3	1.620(3)
P-N2	1.636(3)	P-N4	1.618(3)
	Bond Angles (deg)		
N2-P-N3	110.8(2)	C3-N1-C6	118.0(3)
N2-P-N4	113.9(2)	C3-N1-C9	117.6(3)
N3-P-N4	115.5(2)	C6-N1-C9	122.5(3)

($N_{ax}C$). MS (FAB) m/z 305.2 (100, [n-BuSP(NMeCH$_2$CH$_2$)$_3$N]$^+$), 737.3 (1.5, [(n-BuSP(NMeCH$_2$CH$_2$)$_3$N)$_2$I]$^+$).

Reaction of 11 with *i*-PrI. To a solution of **11** (0.050 g, 0.20 mmol) in acetonitrile (5 mL) was added *i*-PrI (0.5 mL). The solution was stirred at 50 °C for 84 h and evaporated in vacuo to give only the starting material **11**, as shown by ^{1}H NMR spectroscopy.

Measurement of Reaction Rates of 4 with RX. To an NMR tube containing **4** (0.063 mmol) and CD_3CN (0.7 mL) was added RX (0.063 mmol). [31] NMR spectra of the reaction mixture were recorded every 5 min. The reaction times for reaction completion were <5 min for MeI and CH_2=$CHCH_2I$, 20 min for *n*-EtI, 35 min for *n*-PrI, 55 min for *n*-BuI, >6 h for *i*-PrI, and >6 h for *n*-PrBr.

Crystal Structure Analysis of 5(I). A colorless crystal of the title compound was attached to the tip of a glass fiber and mounted on the diffractometer for data collection at −5 ± 1 °C. The cell constants for data collection were determined from a list of reflections found by an automated search routine.

Lorentz and polarization corrections were applied. A correction based on a decay in the standard reflections of 2.0% was applied to the data. An absorption correction based on a series of Ψ-scans was applied. The agreement factor for the averaging of the observed reflections was 1.8% (based on F).

The acentric space group $P2_12_12_1$ was indicated initially by systematic absences and intensity statistics.[19] The positions of the atoms were determined by direct methods.[19] All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were found by the difference Fourier technique and were placed at idealized positions 0.95 Å from the attached atom, with isotropic temperature factors set equal to 1.3 times the isotropic equivalent of that atom. The hydrogen atom positions were not refined. Selected bond distances and angles are given Table I.

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Supplementary Material Available: Tables of complete bond lengths and angles, crystal data, and isotropic thermal parameters (7 pages); listing of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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Electron-Deficient Carbocations. Direct Observation of α-Carbonylmethyl Cations by Laser Flash Photolysis†

Linda J. Johnston,*,‡ Patrick Kwong,§ Avshalom Shelemay,§ and Edward Lee-Ruff*,§

Contribution from the Department of Chemistry, York University, North York, Ontario M3J 1P3, Canada, and Steacie Institute for Molecular Science, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada. *Received September 3, 1992*

Abstract: The 9-carbomethoxyfluoren-9-yl cation was generated under stable ion conditions and characterized by spectral data (visible/NMR spectroscopy) and product identification of the benzene and toluene trapping reactions. The laser flash excitation of methyl α-bromodiphenylacetate and methyl 9-bromo-9-fluorenylcarboxylate generated both the corresponding cations and radicals. Rate constants for nucleophilic quenching by alcohols and bromide ion were measured for both the α-carbomethoxy cations and the unsubstituted diphenylmethyl and 9-fluorenyl cations. The results indicated an increase in kinetic stability upon replacement of α-hydrogen by α-carbomethoxy. Direct comparison of quenching rate constants in the same solvent showed an increase in reactivity of the 9-fluorenyl cations relative to the diphenylmethyl cations.

Introduction

Over the past decade, there has been wide interest in carbocations that have the positive charge center directly attached to an electron-withdrawing group.[1] Such cations have been considered as "destabilized carbocations" on electrostatic grounds and were believed to be intrinsically unstable so that they would form only with great reluctance under forcing conditions. However, recent studies[2-11] have shown that such cations can be formed, studied, and used for synthetic applications.

The carbonyl group is electron-withdrawing on the basis of the σ^+ values as measured from cumyl chloride solvolysis data, and yet very small rate-retarding and even rate-enhancing effects have been observed in solvolysis when this group is directly substituted on the potential carbocation center.[1] More recent studies have shown that bimolecular quenching rate constants for carbocations substituted by carbomethoxy and other electron-withdrawing groups such as trifluoromethyl do not vary significantly in com-

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§ York University.

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