Electron-Transfer Nucleophilic Substitution Reactions on Neopentyl- and Phenyl-Substituted Alkyl Chlorides. Effect of the Bridge Length on the Intramolecular Electron-Transfer Catalysis
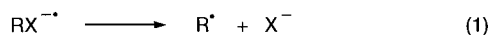
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The nucleophilic substitution reaction of the chlorides RMe_2CCH_2Cl (R = Me, **4**; Ph, **5a**; $PhCH_2$, **5b**) and their relative reactivities toward diphenyl phosphide ions were studied under irradiation in liquid ammonia. The relative reactivities determined were $k_{5a}/k_4 \cong 9$ and $k_{5b}/k_4 \cong 0.85$. These reactions are proposed to occur through the $S_{RN}1$ mechanism. The higher reactivity of **5a** is explained on the basis of its higher electron affinity due to the phenyl substitution and the efficient intramolecular electron transfer from this group to the C–Cl σ^* bond (intra-ET catalysis). Although **5b** also has a phenyl ring, its lower reactivity is ascribed to a decrease in the rate of the intra-ET by elongation of the bridge in one methylene unit. The relative reactivity of **5a** versus **5b** ($k_{5a}/k_{5b} \cong 6.4$) is proposed to indicate the ratio of the intra-ET rates of the radical anions of both compounds. AM1 calculations performed on the system are in agreement with the experimental results.

It is known that neopentyl halides have a low reactivity toward nucleophilic substitutions by polar mechanisms.[1] They belong to a family of aliphatic compounds (neopentyl, cycloalkyl, and bicycloalkyl halides) that can be substituted through the $S_{RN}1$ mechanism.[2] Substitution of neopentyl bromide can be achieved with the nucleophiles PhS^-, Se^{2-}, Ph_2P^-, and Ph_2As^- under photostimulation in liquid ammonia.[3] Carbanions such as the enolate ion of acetophenone react with neopentyl iodide in DMSO under irradiation[4] or in the presence of $FeBr_2$.[5] The propagation cycle of this mechanism is presented in the following equations:

$$RX^{-\bullet} \longrightarrow R^{\bullet} + X^- \qquad (1)$$

$$R^{\bullet} + Nu^- \longrightarrow RNu^{-\bullet} \qquad (2)$$

$$RNu^{-\bullet} + RX \longrightarrow RNu + RX^{-\bullet} \qquad (3)$$

$$RNu^{-\bullet} + RX \longrightarrow RNu + R^{\bullet} + X^- \qquad (1,3)$$

The radical anion of the substrate ($RX^{-\bullet}$) is usually formed in the initiation step by a photostimulated electron transfer (ET) from the nucleophile.[2] This reaction is proposed as dissociative for unsubstituted and unstrained aliphatic halides,[2b,6] leading directly to the aliphatic radical and the anion of the leaving group (eq 1,3). Formation of the uncyclized **2** and cyclized **3** substitution products in the reactions of the radical probes **1a**–**c** with PhS^-, Ph_2P^-, or Me_3Sn^- ions has been used as evidence of the presence of radicals as intermediates in these reactions (eq 4).[7]

1a, Z=CH_2, X = Br
1b, Z=O, X=Br
1c, Z=CH_2, X=I

$$(4)$$
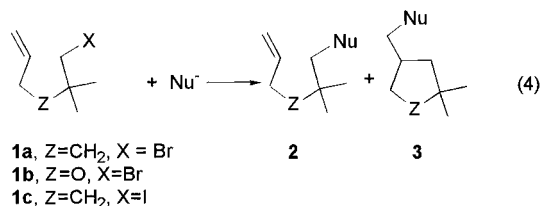
In those cases in which a better acceptor group is present in the molecule in addition to the C–halogen bond, the reactivity can be increased as a result of an intramolecular ET (intra-ET) catalysis. For example, it has been shown that 2-oxo-3,3-dimethyl-bicyclo[2.2.2]oct-1-yl chloride[8] and 2- and 3-oxo-bicyclo[2.2.1]hepta-1-yl chlorides[9] react with Ph_2P^- ions under irradiation by the $S_{RN}1$ mechanism, whereas the unsubstituted chloro compounds do not react under the same experimental conditions.

When a π acceptor such as an aromatic ring is present in the substrate, the intermolecular ET (inter-ET) could form a radical anion intermediate with the extra electron localized in the π^* system (eq 5). The intra-ET from this

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(2) For reviews on aliphatic $S_{RN}1$, see: (a) Rossi, R. A.; Pierini, A. B.; Palacios, S. M. *Advances in Free Radical Chemistry*; Tanner, D. D., Ed.; JAI Press: Greenwich, CT, 1990; p 193; *J. Chem. Educ.* **1989,** *66,* 720. (b) Savéant, J. M. *Adv. Phys. Org. Chem.* **1990,** *26,* 1. (c) Rossi, R. A.; Pierini, A. B.; Peñéñory, A. B. In *The Chemistry of Functional Group*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1995; Supl. D2, Chapter 24.

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(7) (a) Beckwith, A. L. J.; Palacios, S. M. *J. Phys. Org. Chem.* **1991,** *4,* 404. (b) Ashby, E. C.; Gurumurthy, R.; Ridlehuber, R. W. *J. Org. Chem.* **1993,** *58,* 5832. (c) Ashby, E. C.; Deshpande, A. K. *J. Org. Chem.* **1994,** *59,* 7358.

(8) Santiago, A. N.; Takeuchi, K.; Ohga, Y.; Nishida, M.; Rossi, R. A. *J. Org. Chem.* **1991,** *56,* 1581.
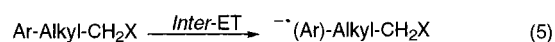
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**Table 1. Reaction of 4, 5a, and 5b with Diphenylphospide Anion[a]**

expt	substrate, M × 10³	Cl⁻ (%)	substitution products[b] (%)
1[c]	**4**, 4.0	80	74
2	**5a**, 3.33	74	70 (61)[d]
3[e]	**5a**, 3.33	<5	f
4[g]	**5a**, 3.33	<5	f
5	**5b**, 4.00	53	49 (32)[d]
6[e]	**5b**, 4.00	<5	f
7[g]	**5b**, 4.00	<5	f

[a] Reactions performed in liquid ammonia (300 mL). Ph_2P^- ions with the same concentration of the substrates. Irradiation time 240 min. The substrates **5a** and **5b** were dissolved in 6 mL of DMSO when added. [b] Quantified by GLC. [c] Ref 3a. [d] Isolated yield. [e] Dark reaction. [f] No substitution product was detected. [g] Reaction performed in the presence of *p*-DNB.

system to the σ^* C–halogen bond will be responsible for the fragmentation of the intermediate into radicals (eq 6).[10]

$$Ar\text{-}Alkyl\text{-}CH_2X \xrightarrow{\textit{Inter-ET}} {}^{-\bullet}(Ar)\text{-}Alkyl\text{-}CH_2X \quad (5)$$

$$ {}^{-\bullet}(Ar)\text{-}Alkyl\text{-}CH_2X \xrightarrow{\textit{Intra-ET}} Ar\text{-}Alkyl\text{-}CH_2{}^\bullet + X^- \quad (6)$$

To get new insights on intra-ET reactions and the effect of the spacer length,[11] we decided to study the relative reactivity of 1-chloro-2,2-dimethyl-propane (neopentyl chloride (**4**)), 1-chloro-2-methyl-2-phenyl propane (neophyl chloride (**5a**)), and 1-chloro-2,2-dimethyl-3-phenyl propane (**5b**) toward Ph_2P^- ions under irradiation.
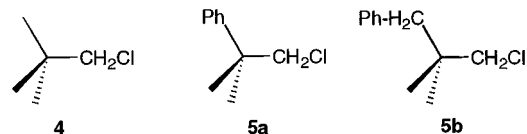

The first member of the series is a simple neopentyl chloride. In **5a**, a methyl group of compound **4** is replaced by a phenyl group, whereas in **5b**, the methyl group is replaced by a benzyl group, so the length of the spacer is increased by one methylene unit. The family thus offers the possibility to study the effect of the π substitution on a simple alkyl halide and the effect of the spacer length on the intra-ET reaction when it is mediated by a flexible chain.

Results

Compounds **4**,[3a] **5a**, and **5b** reacted with Ph_2P^- ions under irradiation to give, after oxidation, the substitution compounds **6**, **7a**, and **7b**, respectively (eq 7) (Table 1, expts 1, 2, 5).

The reactions of **5a** and **5b** did not occur in the dark, and when photostimulated, they were inhibited by the
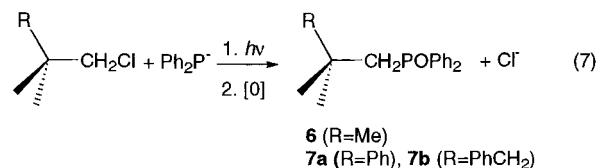
presence of *p*-DNB (Table 1, expts 3, 4, 6, 7). These compounds are proposed to react by the $S_{RN}1$ mechanism.

Relative Reactivities. The relative reactivities of pairs of compounds toward the same nucleophile were determined in reactions in which both substrates were present in excess with respect to the nucleophile. Even though **4** and **5a** had similar reactivity with Ph_2P^- ions in separated experiments, low substitution yield was obtained with **4** when both substrates reacted in an approximately 1:1 ratio. An average relative reactivity $k_{5a}/k_4 \cong 9$ was obtained from reactions with higher **4** to **5a** ratios (Table 2, expts 1–6) following the equation previously reported.[12] A relative reactivity $k_{5b}/k_4 = 0.85$ was determined in competition reactions of **5b** and **4** (Table 2, expts 7–10). Competition experiments between **5a** and **5b** led to the determination of a relative reactivity $k_{5a}/k_{5b} \cong 6.4$ (Table 2, expts 11–13).

Discussion

Semiempirical AM1 calculations[13] were performed to obtain information about the LUMO MOs of the compounds under study, which can be correlated with their reduction potentials,[14] and the intermediates formed in the inter-ET reaction.[15] The calculated LUMO of **4** (1.52 eV) belongs to the σ^* C–Cl bond and is of higher energy than the π LUMOs of compounds **5a** and **5b** (0.31 and 0.37 eV, respectively). Furthermore, the anionic surface of **4** showed an exothermic dissociative behavior with a stabilization zone corresponding to the electrostatic loose complex of the dissociated species (C–Cl distance ≈ 3.8 Å).[16]

On the basis of the calculated LUMOs, **5a** and **5b** will be reduced more easily than **4**, and their π radical anions could be formed in this step. These intermediates, which

(10) Experimental and theoretical data have been used to support the existence of π and σ radical anions. See: (a) Clarke, D. D.; Coulson, C. A. *J. Chem. Soc. A* **1969**, 169. (b) Dressler, R.; Allan, M.; Haselbach, E. *Chimia* **1985**, *39*, 385. (c) Symons, M. C. R. *Acta Chem. Scand.* **1997**, *51*, 127. (d) Pierini, A. B.; Duca, J. S., Jr. *J. Chem. Soc., Perkin Trans. 2* **1995**, 1821. (e) Casado, J.; Gallardo, I.; Moreno, M. *J. Electroanal. Chem.* **1987**, *219*, 197. (f) Andrieux, C. P.; Savéant, J. M.; Zann, D. *Nouv. J. Chim.* **1984**, *8*, 107.

(11) (a) Newton, M. D. *Chem. Rev.* **1991**, *91*, 767. (b) Jordan, K. D.; Paddon-Row, M. N. *Chem. Rev.* **1992**, *92*, 395. (c) Paddon-Row, M. N. *Acc. Chem. Res.* **1994**, *27*, 18. (d) Kuki, A. *Structure and Bonding*; Springer-Verlag: Berlin, 1991; p 50. (e) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265. (f) Isied, S. S.; Ogawa, M. Y.; Wishart, J. F. *Chem. Rev.* **1992**, *92*, 381. (g) Beratan, D. N.; Betts, J. N.; Onuchic, J. N. *Science* **1991**, *252*, 12.

(12) The equation used in the relative reactivity determination of pairs of substrates toward a nucleophile is:

$$k_1/k_2 = \ln([RX_1]_0/[RX_1]_t)/\ln([RX_2]_0/[RX_2]_t)$$

where $[RX_1]_0$ and $[RX_2]_0$ are initial concentrations and $[RX_1]_t$ and $[RX_2]_t$ are concentration at time t of both substrates. This equation is based on a first-order reaction of both substrates with the nucleophile. See: Bunnett, J. F. In *Investigation of Rates and Mechanisms of Reaction*, 3rd ed.; Lewis, E. S., Ed.; Wiley-Interscience: New York, 1974; part 1, p 159.

(13) All the calculations were carried out with complete geometry optimization, and the semiempirical AM1 method as implemented in AMPAC. See: Liotard, D. A.; Healy, E. F.; Ruiz, J. M.; Dewar, M. J. S. AMPAC version 2.1, Quantum Chemistry Program Exchange, program 506. *QCPE Bull.* **1989**, *9*, 123.

(14) Pierini, A. B.; Santiago, A. N.; Rossi, R. A. *Tetrahedron* **1991**, *47*, 941.

(15) (a) The AM1/UHF stationary points were characterized by calculating their Hessian matrix, no negative eigenvalue for a minimun energy structure, and one negative eigenvalue for a transition state. (b) The CI calculations were performed with the AM1/RHF Hamiltonian within the subspace of all possible excitations of five electrons into five molecular orbitals, from SOMO-2 up to SOMO+2 (CI = 5).

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Table 2. Competition Reactions of the Pairs of Substrates (5a:4), (5b:4), and (5a:5b) toward Diphenyl Phosphide Anion[a]

expt	substrates, $M \times 10^3$	substitution products (%)[b,c]	relative reactivity	average
1	**5a**, 1.96; **4**, 16.4	**7a** (27); **6** (32)	$k_{5a}/k_4 = 8.1$	
2	**5a**, 1.80; **4**, 20.0	**7a** (26); **6** (34)	$k_{5a}/k_4 = 9.4$	
3	**5a**, 1.84; **4**, 24.0	**7a** (32); **6** (52)	$k_{5a}/k_4 = 9.2$	
4[d]	**5a**, 1.76; **4**, 24.3	**7a** (6); **6** (9)	$k_{5a}/k_4 = 8.8$	
5	**5a**, 1.78; **4**, 28.0	**7a** (29); **6** (62)	$k_{5a}/k_4 = 8.2$	
6	**5a**, 1.84; **4**, 32.2	**7a** (31); **6** (65)	$k_{5a}/k_4 = 9.5$	$k_{5a}/k_4 =$ 8.9 ± 0.6
7	**5b**, 1.79; **4**, 2.48	**7b** (16); **6** (26)	$k_{5b}/k_4 = 0.87$	
8	**5b**, 1.79; **4**, 3.19	**7b** (27); **6** (53)	$k_{5b}/k_4 = 0.89$	
9	**5b**, 2.55; **4**, 1.88	**7b** (45); **6** (40)	$k_{5b}/k_4 = 0.81$	
10	**5b**, 3.24; **4**, 1.82	**7b** (47); **6** (31)	$k_{5b}/k_4 = 0.83$	$k_{5b}/k_4 =$ 0.85 ± 0.04
11[e,f]	**5a**, 4.41; **5b**, 3.65	**7a** (36); **7b** (5.4)	$k_{5a}/k_{5b} = 6.2$	
12[f]	**5a**, 1.89; **5b**, 1.56	**7a** (56); **7b** (8.5)	$k_{5a}/k_{5b} = 6.8$	
13[f,g]	**5a**, 0.50; **5b** 0.39	**7a** (57); **7b** (8.1)	$k_{5a}/k_{5b} = 6.1$	$k_{5a}/k_{5b} =$ 6.4 ± 0.4

[a] Performed in liquid ammonia−DMSO 3%. Irradiation time (180 min or less if the solution turns colorless). Ph_2P^- (1.6×10^{-3} M). [b] Calculated with respect to the mmoles of nucleophile. [c] Quantified by GLC. [d] Shorter reaction time; quenched in the presence of Ph_2P^-. [e] Ph_2P^- (3.1×10^{-3} M). [f] Duplicated run. [g] Ph_2P^- (0.37×10^{-3} M).
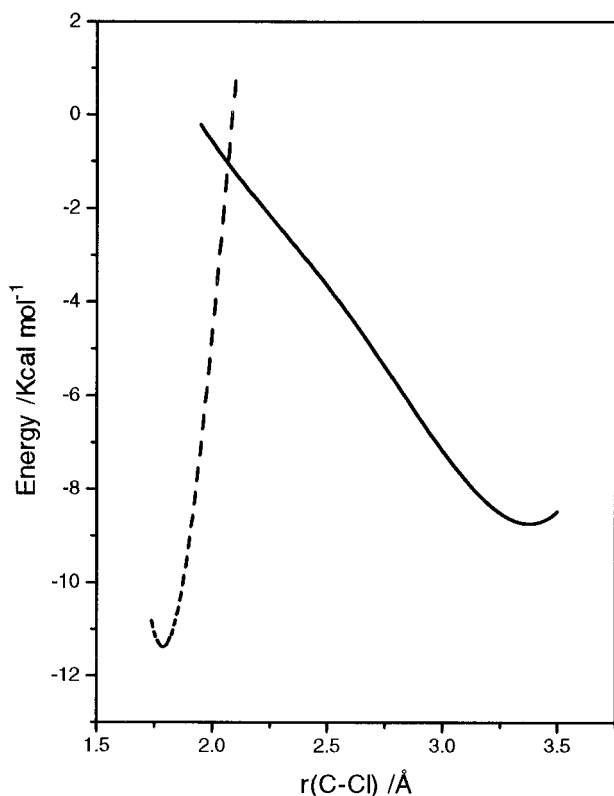

Figure 1. AM1/UHF potential surface for the intra-ET reaction of $5a^{-\bullet}$ (taken as representative): π radical anion (dashed line); σ anionic surface (solid line).

have the negative charge and unpaired spin density on the phenyl ring,[10d] were characterized as the most stable form of both radical anions (**5a**$^{-\bullet}$ and **5b**$^{-\bullet}$ henceforth) at the AM1/UHF and RHF/CI level.[15] The intra-ET of these intermediates from the phenyl ring to the C−Cl bond to give radicals occurs through the avoided crossing of their π potential surface with the surface of the dissociated anionic species, as shown in Figure 1 for **5a**$^{-\bullet}$, taken as representative.
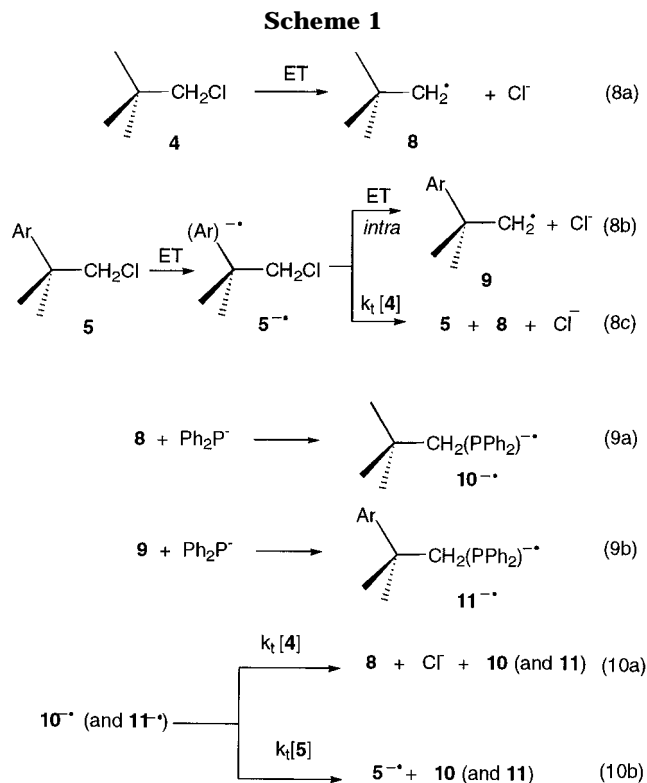
Scheme 1

On the basis of these calculations and the $S_{RN}1$ propagation cycle, the mechanistic steps in Scheme 1 can be proposed for competition reactions of compounds **5a** or **5b** and **4** toward a given nucleophile.

The dissociative ET to **4** affords neopentyl radical **8** (eq 8a). On the other hand, the ET to compounds **5** can form the radical anion **5**$^{-\bullet}$ (π type). Two reactions can be proposed for **5**$^{-\bullet}$, intra-ET to give the phenyl-substituted radicals **9** (eq 8b) and inter-ET to **4** (8c).

Radicals **8** and **9** react with Ph_2P^- to form radical anions **10**$^{-\bullet}$ and **11**$^{-\bullet}$, respectively (eqs 9a and 9b). Both reactions are estimated to occur at similar rates, because they involve the coupling of similar radicals with the same nucleophile to form radical anions of similar stability (the extra electron would be located at the PPh$_2$ group). These radical anions can transfer the extra electron to the substrates to form the substitution products **10** and **11** and the intermediates that will continue the propagation cycle.

On the basis of the mechanism proposed and the higher electron affinity of **5a** and **5b** compared to that of **4** toward the inter-ET steps of the propagation cycle (eqs 10), the difference in relative reactivity between these compounds and **4** would depend mainly on the differences in the intra-ET rates of their radical anions. The higher reactivity of **5a** ($k_{5a}/k_4 \cong$ **9**) with respect to **5b** ($k_{5b}/k_4 \cong$ 0.85) is thus indicating that the intra-ET reaction is faster for **5a**$^{-\bullet}$. The elongated bridge that mediates the reaction in **5b**$^{-\bullet}$ increases the lifetime of this intermediate, favoring its inter-ET reaction to **4** (eq 8c), which thus has a similar reactivity to **5b**.

In the competition reactions between **5a** and **5b**, the relative reactivity also will depend on the relative fragmentation rate of their radical anions. As both compounds have similar reduction potentials, the rate of formation of the intermediates will be similar. The fact that **5a** is more reactive than **5b** indicates that in this

system an inter-ET between them and their radical anions can be proposed to occur as a reversible reaction with similar rates in both senses (exchange reaction) (eq 11).[17]
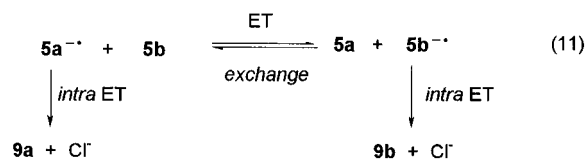
In addition to this exchange reaction, **5a**$^{-\bullet}$ and **5b**$^{-\bullet}$ will render, by intra-ET, the radicals **9a** and **9b**, respectively. Both radicals can react with Ph_2P^- ions at similar rates to afford ultimately the substitution compounds. At equilibrium, the determined $k_{5a}/k_{5b} \cong 6.4$ (Table 2)[18] is indicative of the ratio of the fragmentation rates of the radical anions of both compounds.[19] In agreement with this experimental reactivity, the semiempirical activation energy evaluated for the intra-ET of **5a**$^{-\bullet}$ and **5b**$^{-\bullet}$ is higher by ca. 2 kcal/mol for the elongated radical anion.

Experimental Section

General Methods. Irradiation was conducted in a reactor equipped with two 400-W lamps emitting maximally at 350 nm (Philips Model HPT, air- and water-refrigerated). HRMS were recorded at the Institute of Advanced Materials Study, Kyushu University, Japan.

Materials. All materials, including neopentyl chloride, neophyl chloride, and 2,2-dimethyl-3-phenyl-1-propanol (Aldrich), were commercially available and were used as received. 1-Chloro-2,2-dimethyl-3-phenylpropane (**5b**) was prepared from 2,2-dimethyl-3-phenyl-propyl tosylate[20] following the procedure described for the neopentyl analogue.[21] The product was isolated as a colorless liquid by chromatography on silica gel with petroleum ether as eluent. ^{1}H NMR (acetone-d_6) δ 0.98 (6H, s), 2.67 (2H, s), 3.39 (2H, s), 7.16–7.36 (5H, m); ^{13}C NMR δ 25.31, 36.38, 44.79, 54.74, 126.22, 127.94, 130.39, 137.99; MS (EI+) 182, 147, 133, 105, 91, 77; HRMS calcd for $C_{11}H_{15}Cl$ 182.0862, found 182.0863.

(17) Although there is no experimental data on the electron self-exchange reaction between the benzene radical anion and benzene, it has been calculated to be 1.4×10^9 at 298 K. See: Formosinho, S. J.; Arnaut, L. G. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 977. For exchange reaction of other aromatic radical anions, see: Ward, R. L.; Weissman, S. I. *J. Am. Chem. Soc.* **1954**, *76*, 3612. Bergman, I. *Trans. Faraday Soc.* **1954**, *50*, 829.

(18) This value is expected to decrease to $k_{5a}/k_{5b} \cong 1$ under high dilution, conditions where the equilibrium is not attained, according to simulations performed with the program *Chemical Kinetics Simulator* 1.01 (International Business Machines Corporation, 1996). We were unable to reach this limit experimentally.

(19) On the basis of the proposed mechanism and under equilibrium conditions, the relative rate of formation of the substitution products **11a** and **11b** simplified to the following integrated equation:

$$k_{\text{frag}5a^-}/k_{\text{frag}5b^{-\bullet}} = K_{\text{exchange}} \, (\ln([5a]_0/[5a]_t)/\ln([5b]_0/[5b]_t))$$

(20) Bordwell, F. G.; Pitt, B. M.; Knell, N. *J. Am. Chem. Soc.* **1951**, *73*, 5004. Beringer, F. M.; Schultz, H. S. *J. Am. Chem. Soc.* **1955**, *77*, 5533.

(21) Stephenson, B.; Solladié, G.; Mosher, H. S. *J. Am. Chem. Soc.* **1972**, *94*, 4184.

Photostimulated Reaction of 5b with Ph₂P⁻ in Liquid Ammonia. The following procedure is representative of all the reactions. Into a three-necked round-bottomed flask equipped with a coldfinger condenser charged with dry ice–ethanol, a nitrogen inlet, and a magnetic stirrer was condensed 300 mL of ammonia previously dried with Na metal under nitrogen. Ph₃P (1.6 mmol) and Na metal (3.2 mmol) were added to form Ph₂P⁻ ions, and *t*-BuOH (3.2 mmol) was added to neutralize the amide ions formed. To this solution was added **5b** (1.6 mmol), dissolved in 6 mL of DMSO (stored under 4 Å molecular sieves), and then the solution was irradiated for 240 min. The reaction was quenched by adding ammonium nitrate in excess, and the ammonia was allowed to evaporate. The residue was dissolved with water and extracted twice with Cl_2-CH_2 (20 mL each). The products were oxidized with H_2O_2 and then quantified by GLC with the internal standard method.

The same procedure was followed when the reaction was performed in the presence of *p*-DNB, except that 20 mol % *p*-DNB was added to the solution of nucleophile prior to the substrate addition.

Photostimulated Competition Reaction of 5a and 5b with Ph₂P⁻. The procedure was similar to that previously described, except that both substrates were added, dissolved in DMSO, to the solution of nucleophile in liquid ammonia.

(2,2-Dimethylpropyl)diphenylphosphine Oxide (6). Isolated and characterized as described[3b] by comparison with an authentic sample.

(2-Methyl-2-phenylpropyl)diphenylphosphine Oxide (7a). White solid isolated by column chomatography on silica gel (petroleum ether–diethyl ether as eluent) and recrystallized from hexane–acetone: mp 134–135 °C; ^{1}H NMR (acetone-d_6) δ 1.53 (6H, s), 2.83 (2H, d), 6.93–7.87 (15H, m); ^{13}C NMR δ 29.84, 29.92, 38.24, 38.33, 42.70, 44.06, 125.98, 126.07, 128.20, 128.52, 128.76, 130.68, 130.86, 131.21, 135.68, 137.60, 149.44, 149.61; MS (EI+) 334, 278, 277, 257, 215, 202, 201, 183, 152, 133, 119; HRMS calcd for $C_{22}H_{23}OP$ 334.1480, found 334.1484.

(2,2-Dimethyl-3-phenylpropyl)diphenylphosphine Oxide (7b). White solid isolated by chromatography on silica gel (petroleum ether–diethyl ether as eluent) and recrystallized from hexane–acetone: mp 139–141 °C; ^{1}H NMR (acetone-d_6) δ 1.03 (6H, s), 2.42 (2H, d), 2.87 (2H, s), 7.10–7.97 (15H, m); ^{13}C NMR δ 28.68, 28.83, 35.99, 36.08, 39.24, 40.63, 49.45, 49.60, 126.42, 128.08, 128.79, 128.99, 130.74, 130.92, 131.39, 131.45, 131.51, 136.30, 138.22, 139.29; MS (EI+) 348, 257, 215, 201, 183, 154, 125, 91, 77; HRMS calcd for $C_{23}H_{25}OP$ 348.1634, found 348.1634.

Supporting Information Available: AM1/UHF heat of formation for the stationary points calculated, equilibrium geometries of **5a**$^{-\bullet}$, **5b**$^{-\bullet}$, potential surfaces for the intra-ET of **5b**$^{-\bullet}$ and the dissociative inter-ET to **4**, and ^{1}H and ^{13}C NMR for **5b**, **7a**, and **7b**. This material is available free of charge via the internet at http://pubs.acs.org.

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