JOC
The Journal of
Organic Chemistry

VOLUME 66, NUMBER 10 MAY 18, 2001

Articles

Dramatic Effect of the Metal Cation in Dealkylation Reactions of Phosphinic Esters Promoted by Complexes of Polyether Ligands with Metal Iodides

Domenico Albanese, Dario Landini, and Angelamaria Maia*

Centro CNR and Dipartimento di Chimica Organica e Industriale,
Via Venezian 21, I-20133 Milano, Italy

angelamaria.maia@unimi.it

Received September 7, 2000

Metal ion electrophilic catalysis has been revealed in dealkylation reactions of phosphinic esters **1**−**4** promoted by complexes of polyether ligands **5**−**7** with metal iodides MI_n ($M^{n+} = Li^+$, Na^+, K^+, Rb^+, Ca^{2+}, Sr^{2+}, Ba^{2+}) in low polarity solvents (chlorobenzene, 1,2-dichlorobenzene, and toluene) at 60 °C. The catalytic effect increases with increasing the Lewis acid character of the cation, in the order $Rb^+ < K^+ < Na^+ < Li^+$ and $Ba^{2+} < Sr^{2+} < Ca^{2+}$. The results are interpreted in terms of a transition state where the complexed cation ($M^{n+} \subset$ Lig) assists the departure of the leaving group $Ph_2P(O)O^-$ and, at the same time, favors the attack at carbon of the nucleophile I^- ("push−pull" mechanism). The rate sequence found for **1**−**4** (Me > Et ≫ *i*-Pr and *t*-Bu) shows that this reaction can be utilized for the selective dealkylation of these substrates.

Introduction

In recent years, increasing interest has been focused on the production of compounds, analogues of the nucleic acids, with modified internucleosidic bonds such as alkyl phosphotriesters and methylphosphinates of oligonucleotides.[1] In the synthesis of oligonucleotides with the phosphotriester method, the key step is often represented by the final removal of the protective group, usually a methyl group, from the phosphoric function of the substrate.[2] The selectivity of this reaction, expressed as the ratio between the attack at phosphorus (phosphorylation) and at carbon (dealkylation), largely depends on the nucleophile used. Whereas nucleophiles with a high charge density such as hydroxides, alkoxides, enolates, etc. preferentially attack the phosphorus, more polarizable nucleophiles, like bromides or iodides, yield products mainly arising from nucleophilic attack at carbon.[3] The selectivity obtained in solution can be, however, completely reversed in the gas phase where, in the absence of any solvation, it is possible to measure the intrinsic reactivity of carbon versus phosphorus.[3]

By contrast, the effect of the counterion was only qualitatively reported in a few publications and just for divalent cations.[4,5] Later on, Buncel et al. revealed and quantitatively evaluated for the first time the participation of the metal cation ("electrophilic catalysis") in reactions of nucleophilic substitution at phosphorus of phosphoric esters by ethoxides[6] and phenoxides[7] of alkali

---

[1] Koole, L. H.; Moody, H. M.; Broeders, N. L.; Quaedflieg, P. J.; Kuijpers, W. H.; van Genderen, M. H.; Coenen, A. J.; van der Wal, S.; Buck, H. M. *J. Org. Chem.* **1989**, *54*, 1657.

[2] Smith, D. J.; Ogilvie, K. K.; Gillen, M. F. *Tetrahedron Lett.* **1980**, *21*, 861.

[3] Lum, R. C.; Grabowski, J. J. *J. Am. Chem. Soc.* **1992**, *114*, 8619.

[4] Steffens, J. J.; Sampson, E. J.; Siewers, I. J.; Benkovic, S. J. *J. Am. Chem. Soc.* **1973**, *95*, 936.

[5] Wadsworth, W. S., Jr. *J. Org. Chem.* **1981**, *46*, 4080.

[6] Dunn, E. J.; Buncel, E. *Can. J. Chem.* **1989**, *67*, 1440.

10.1021/jo0056388 CCC: $20.00

metals in ethanol. The catalytic effect depends on the metal ion, increasing in the order $K^+ < Na^+ \ll Li^+$. More recently, we found an analogous behavior in nucleophilic substitution reactions of alkylsulfonates promoted by complexes of crown ethers and polyethylenglycols with metal salts in chlorobenzene.[8,9]

In the present work, a kinetic study of the effect of the metal cation on the dealkylation rate of alkyl diphenylphosphinates **1**−**4** by complexes of polyether ligands **5**−**7** with alkali and alkaline-earth metal iodides in low polarity media (chlorobenzene,1,2-dichlorobenzene, and toluene) is reported. A comparative study of the corresponding uncatalyzed reactions with bulky quaternary onium iodides has also been included.

Results and Discussion

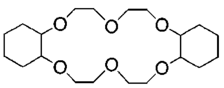
Kinetics were performed by reacting comparable amounts of alkyl diphenylphosphinates **1**−**4** (0.006−0.03 M) and preformed $(M^{n+} \subset Lig)nI^-$ complex (0.002−0.014 M) in the appropriate solvent (chlorobenzene, 1,2-dichlorobenzene, toluene) at 60 ± 0.1 °C (eq 1).

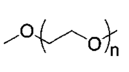
$$\underset{\mathbf{1\text{-}4}}{n\,Ph_2P(O)OR} + (M^{n+} \subset Lig)nI^- \longrightarrow (M^{n+} \subset Lig)nPh_2P(O)O^- + n\,RI \qquad (1)$$

n = 1,2 R = Me (**1**), Et (**2**), *i*-Pr (**3**), *t*-Bu (**4**)

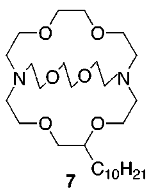
$M^{n+} = Li^+, Na^+, K^+, Rb^+, NH_4^+, Ca^{2+}, Sr^{2+}, Ba^{2+}$

Lig = PHDB18crown 6 (**5**); PEG400Me$_2$ (**6**); [2.2.2, C$_{10}$] (**7**)


5



6



7

Rates have been measured by potentiometric titration of the complexed iodide and/or by gaschromatographic determination of the unreacted substrate **1**−**4** evaluated with respect to an internal standard (tetradecane). Under these conditions reactions follow a regular second-order kinetic eq 2 up to at least 3 half-life times (Figure 1). Results are reported in Tables 1−3.

$$\text{rate} = k[\text{substrate}][\text{complexed I}^-] \qquad (2)$$

In the case of K^+, Rb^+, and NH_4^+, the reaction 1 goes to the equilibrium (3) already for low conversion values (<20%). The equilibrium can be fully shifted toward the formation of the dealkylation product by addition, in the reaction medium, of equimolar quantities, with respect to the $(M^{n+} \subset Lig)nI^-$ complex, of triethylamine.

$$\underset{\mathbf{1\text{-}4}}{n\,Ph_2P(O)OR} + (M^{n+} \subset Lig)nI^- + n\,Et_3N \rightleftharpoons (M^{n+} \subset Lig)nPh_2P(O)O^- + n\,Et_3N^+RI^-\downarrow \qquad (3)$$

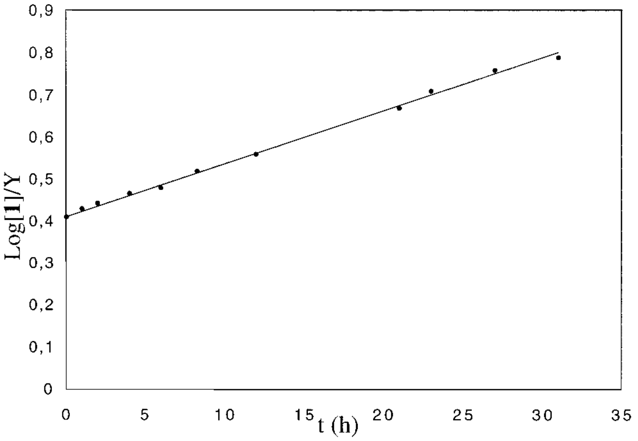


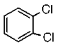
Figure 1. Second-order plot for the reaction of methyl diphenylphosphinate **1** (0.025 M) with $(Na^+ \subset PHDB18C6)I^-$ (0.0095 M) in chlorobenzene, at 60 °C. Y = $[(Na^+ \subset PHDB18C6)I^-]$.

Table 1. Second-Order Rate Constants *k* ($M^{-1}\,s^{-1}$) for the Dealkylation of Alkyl Diphenylphosphinates $Ph_2P(O)OR$ (R = Me, Et, *i*-Pr, *t*-Bu) 1−4 by Complexes $(M^+ \subset Lig)I^-$ (Lig = 5 and 7) in Chlorobenzene, at 60 °C[a]

	R	M^+	ρ (Å^{-1})	ligand	10^3k[b] ($M^{-1}\,s^{-1}$)	k_{rel}	$-\Delta G_{cat}$[c] (kcal mol^{-1})
1	Me	Rb^+	0.67	**5**	0.029	1	3.8
1	Me	K^+	0.75	**5**	0.061(0.23)[d]	2.1	4.3
1	Me	Na^+	1.02	**5**	0.63	21.7	5.8
1	Me	Li^+	1.28	**5**	5.6	193	7.3
				7	0.084		
2	Et	Li^+	1.28	**5**	0.064		
3	*i*-Pr	Li^+	1.28	**5**	*e*		
4	*t*-Bu	Li^+	1.28	**5**	*e*		

[a] A chlorobenzene solution (30 mL) of substrates **1**−**4** (0.02−0.03M) and $(M^+ \subset Lig)I^-$ complex (0.009−0.014 M). [b] Average of at least two determinations. The error in these values is estimated to be 5%. [c] $\Delta G_{cat} = \Delta G^{\ddagger}_{cat} - \Delta G^{\ddagger}_{uncat} = -RT \ln (k_{cat}/k_{uncat})$; see Figure 2 for determination of k_{uncat}. [d] Value obtained by using NH_4^+. [e] No reaction after 2 weeks.

Table 2. Effect of Solvent Polarity on the Second-Order Rate Constant of the Demethylation of 1 with $(M^+ \subset Lig)I^-$ Complexes, at 60 °C[a]

		$10^3k(M^{-1}s^{-1})$[b]		
		PHDB18C6 **5**		PEG400Me$_2$ **6**
solvent	E_T^N[c]	Li^+	Na^+	Li^+
toluene	0.099	15.8 (7.4)	2.1 (10.5)	[d] [d]
PhCl	0.188	5.3 (2.5)	0.71 (2.5)	10.9 (3)
	0.225	2.1 (1)	0.2 (1)	3.7 (1)

[a] A solution (30 mL) of substrate (0.015−0.03M) and $(M^+ \subset Lig)I^-$ complex (0.005−0.013M). [b] Average of at least two determinations. The error is estimated to be 5%. [c] See ref 12. [d] The extent of complexation is very low (≤2%).

The latter, in fact, reacts with the alkyl iodide formed to give the corresponding quaternary ammonium salt $Et_3N^+RI^-$ that quantitatively precipitates during the reaction. Blank experiments performed in parallel have shown that the solubility of $Et_3N^+RI^-$ is negligible in the organic medium.

For having a comparison with the uncatalyzed reaction, the dealkylation (1) has been carried out with the lipophilic quaternary ammonium salt hexyl$_4N^+I^-$ in the presence of an equimolar amount of triethylamine. As expected, the reaction is very slow, and a conversion <10% was found after about 1 month. On the other hand, the use of complexable $NH_4^+I^-$ showed a reduced but still detectable catalysis (Table 1).

---

(7) Dunn, E. J.; Moir, R. Y.; Buncel, E.; Purdon, J. G.; Bannard, R. A. *Can. J. Chem.* **1990**, *68*, 1837.

(8) Gobbi, A.; Landini, D.; Maia, A.; Secci, D. *J. Org. Chem.* **1995**, *60*, 5954.

(9) Gobbi, A.; Landini, D.; Maia, A.; Penso, M. *J. Chem. Soc., Perkin Trans. 2* **1996**, 2505 and references therein.

Table 3. Second-Order Rate Constants k (M^{-1} s^{-1}) for the Demethylation of Methyl Diphenylphosphinate 1 by Complexes ($M^{2+} \subset$ PHDB18C6)$2I^-$ in Chlorobenzene at 60 °C[a]

M^{2+}	ρ ($Å^{-1}$)	10^3 k (M^{-1} s^{-1})[b]	k_{rel}
Ba^{2+}	1.40	0.46	1
Sr^{2+}	1.57	6.24	13.6
Ca^{2+}	1.89	61.7	134

[a] A chlorobenzene solution (30 mL) of substrate (0.006−0.008M) and complexed iodide (0.002−0.005M). [b] Average of at least two determinations. The error is estimated to be ≤10%.

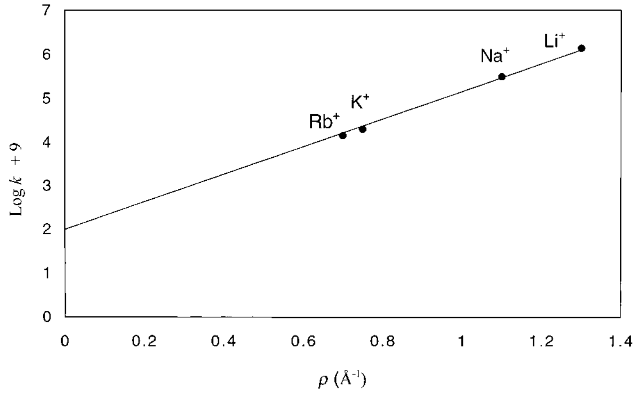


Figure 2. Correlation between second-order rate constant k (M^{-1} s^{-1}) and charge density ρ ($Å^{-1}$) of the cation in the demethylation reaction of methyl diphenylphosphinate **1** with complexes ($M^+ \subset$ PHDB18C6)I^-, where $M^+ = Li^+$, Na^+, K^+, Rb^+, in chlorobenzene ($r = 0.9999$, $k_{uncat} = 9.35 \times 10^{-8}$ (M^{-1} s^{-1}) extrapolated value for $\rho = 0$).

In addition, the dealkylation rate strongly depends on the alkyl substituent R (R = Me, Et, *i*-Pr, *t*-Bu). As reported in Table 1, the cation being the same, the second-order rate constant k (M^{-1} s^{-1}) decreases about 2 orders of magnitude on changing from the methyl **1** to the corresponding ethyl **2** derivative, and no reaction at all was observed in the case of the corresponding isopropyl **3** and *tert*-butyl **4** phosphinates, even after prolonged times. A very good linear correlation ($r = 0.9999$) was obtained in the demethylation of **1** by plotting the second-order rate constants k (M^{-1} s^{-1}) measured for the series of alkali cations M^+ (Li^+, Na^+, K^+, Rb^+) vs the corresponding charge densities ρ, obtained by dividing the charge z of the cation for its ionic radius r (Figure 2).

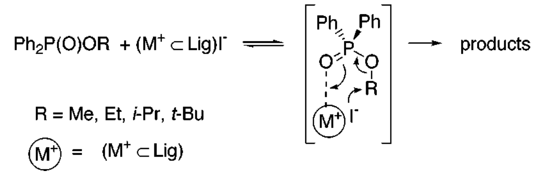
An analogous correlation was also obtained in the case of the alkaline-earth cations Ca^{2+}, Sr^{2+}, and Ba^{2+}. For these divalent cations, however, the corresponding second-order rate constants are lower than those expected from their charge density values (Tables 1 and 3).

Kinetic data as a whole evidence the participation of the metal cation in the dealkylation reaction of alkyl diphenylphosphinates **1** and **2** promoted by complexes of polyethers PHDB18-crown-6 **5** and PEG400Me_2 **6** with metal iodides in low polarity media (eq 1).

Results can be explained in terms of a transition state where the complexed cation ($M^+ \subset$ Lig) can interact with both the ion-paired nucleophile I^- as well as with the leaving group $Ph_2PO_2^-$ (Scheme 1).

In the activation process, the ion-pair ($M^+ \subset$ Lig)I^- reacts following a concerted "push−pull" mechanism where the complexed metal cation ($M^+ \subset$ Lig) stabilizes the developing negative charge on the phosphinic oxygens and at the same time favors the nucleophilic attack of the iodide at the alkylic carbon ("electrophilic catalysis").

Scheme 1



An analogous mechanism was proposed by Buncel in reactions of alkali metal ethoxides with sulfonic and phosphinic esters.[10] The higher the interaction of the complexed cation ($M^+ \subset$ Lig) with the leaving group, the higher must be the reactivity of the iodide and hence the higher the corresponding rate constant. As shown in Table 1, in the demethylation reaction 1 with the series of alkali iodides the second-order rate constants k (M^{-1} s^{-1}) progressively increase, up to about 200 times, in the order $k_{Rb^+} < k_{K^+} < k_{Na^+} \ll k_{Li^+}$. Such a sequence is in line with the increasing interaction of the metal ion with the leaving group $Ph_2PO_2^-$ on increasing the Lewis acidity of the cation ($Rb^+ < K^+ < Na^+ < Li^+$).[11]

The electrophilic catalysis is also confirmed by the excellent ($r = 0.9999$) linear correlation found by plotting the second-order rate constants k (M^{-1} s^{-1}) of the reaction 1 as a function of the charge density ρ of the cation (Figure 2).

In addition, the comparison with the extrapolated value of the rate constant for the uncatalyzed reaction k_{uncat} (M^{-1} s^{-1}) (Figure 2) allows a rough evaluation of the entity of electrophilic catalysis observed in the reaction 1. Interestingly, the catalytic effect ΔG_{cat}, expressed as decrease of the activation free energy $\Delta\Delta G^\ddagger$, is particularly remarkable in this case, passing from 3.8 kcal/mol for Rb^+ up to more than 7 kcal/mol in the case of Li^+ cation where the interaction with the phosphinic oxygens reaches its maximum value (Table 1).

An analogous behavior has been obtained when the demethylation reaction 1 was performed with the complexes of crown ether **5** with alkaline-earth metal iodides MI_2 ($M^{2+} = Ca^{2+}$, Sr^{2+}, Ba^{2+}). Also in this case, the rate constant noticeably increases (up to more than two powers of 10) by increasing the charge density of the cation in the order $Ba^{2+} < Sr^{2+} < Ca^{2+}$ (Table 3). The transition state for divalent cations is substantially the same as that proposed for the monovalent ions M^+ (Scheme 1) and involves only one anion at a time, as confirmed by the reaction order found: first-order both in substrate **1** and in complexed iodide ($M^{2+} \subset$ PHDB18C6)$2I^-$.

The lower reactivity of the latter complexes if compared with that expected from their charge density values (Tables 1 and 3) can likely be attributed to a higher energy of interaction of the divalent cation with the anion within the ion pair in the ground state. A very similar trend was previously observed in nucleophilic substitution reactions promoted by cryptates of metal iodides in low polarity media and explained in the same way.[9]

The variation of reactivity on changing the solvent does not indicate any substantial modification in the transition state with the polarity (Table 2). The cation being the same, the sequence found, $k_{1,2\text{-dichlorobenzene}} < k_{\text{chlorobenzene}}$

---

[10] Pregel, M. J.; Buncel, E. *J. Org. Chem.* **1991**, *56*, 5583 and references therein.

[11] Pearson, R. G. *Coord. Chem. Rev.* **1990**, *100*, 403.

$< k_{\text{toluene}}$, reflects the increasing nucleophilic reactivity of the iodide on diminishing the polarity of the medium.[12]

Conclusions

The results as a whole reveal the fundamental role played by the cation M^{n+} ("electrophilic catalysis") and the alkyl group in determining the dealkylation rate of alkyl diphenylphosphinates **1**−**4** by complexes of polyethers **5** and **6** with alkali and alkaline-earth metal iodides in low polarity solvents. The catalytic effect increases with increasing the Lewis acid character of the cation and is mainly related to the ability of the ligand to effectively shield the metal ion charge.

It is worth noting that cyclic polyethers such as crown ether PHDB18crown6 **5** or open chain as PEG400Me$_2$ **6**, that are anion activators less efficient than macrocyclic cryptands such as [2.2.2,C$_{10}$] **7**,[13,14] play a major role in cation-assisted reactions. Besides solubilizing inorganic salts in low polar media, these ligands form stable inclusion complexes where the metal cation, even if partially shielded by the ethereal oxygens, still keeps a remarkable density of charge and hence can interact with the leaving group $Ph_2PO_2^-$ in the transition state (Scheme 1). Metal ion electrophilic catalysis largely overcomes, particularly for high charge density cations, the lower anion activation realized by ligands **5** and **6** as experimentally confirmed by the comparison with cryptand [2.2.2,C$_{10}$] **7** (Table 1).

The variations of rate constant obtained with these complexed cations ($M^+ \subset$ Lig) in chlorobenzene ($k_{(K^+\subset Lig)}/k_{(Na^+\subset Lig)}/k_{(Li^+\subset Lig)} = 1{:}10{:}92$) are even higher than those found by other authors in analogous demethylation reactions with metal ions M^+ in acetone ($k_{K^+}/k_{Na^+}/k_{Li^+} = 1{:}1.6{:}9$).[15] In dipolar aprotic (acetone) and protic (MeOH) media, where metal salts are soluble as such, metal ions M^+ in equilibrium with ion pairs M^+Y^- can directly interact with the substrate in the transition state. In these systems, the addition of the polyether, which selectively binds the cation[15] or destroys the ion pair,[7] inhibits electrophilic catalysis and is most likely the main reason for the decelerating effect observed.

Finally, the sequence of reactivity obtained for alkyl diphenylphosphinates **1**−**4** with the complexes of LiI (Me > Et ≫ *i*-Pr^i and *t*-Bu) (Table 1) clearly indicates that, from a practical point of view, this reaction can be utilized with success for the selective demethylation of these substrates.

Experimental Section

Methods. ^{1}H and ^{31}P NMR spectra were recorded in CDCl$_3$ on Bruker AC 300 and AMX 300 spectrometers using CHCl$_3$ and aqueous 85% H$_3$PO$_4$ as external references. Potentiometric titrations were performed with a Metrohm 670 titroprocessor by using a combined silver electrode isolated with a potassium nitrate bridge. Karl Fischer determinations were carried out with a Metrohm 684 KF coulometer. GC data were obtained with a Perkin-Elmer 8310 equipped with a 50 × 1/8 in OV-101−5% on chromosorb WHP 100/120 mesh column.

Materials and Solvents. Tetrahexylammonium iodide, ligands PHDB18C6 **5**, PEG 400Me$_2$ **6** and [2.2.2,C$_{10}$] **7** were commercial products, utilized as purchased. Metal and ammonium iodides were Analar grade commercial products used as such after dehydration of the salt in an oven, at 110−120 °C, under vacuum for several hours. In all cases the water content is $\leq$0.05 mol of H$_2$O per mol of salt (Karl Fischer titration). Dry (Fluka) chlorobenzene, 1,2-dichlorobenzene and toluene (H$_2$O $\leq$ 15 ppm) were used. Alkyl diphenylphosphinates Ph$_2$P(O)OR **1**−**4** were prepared by reacting diphenylphosphinyl chloride and the corresponding alcohol in the presence of triethylamine in CH$_2$Cl$_2$ following a previously reported procedure.[16]

Data for **1** (R = Me): white hygroscopic solid; mp 56−58 °C [lit.[16] bp 178 °C (2.4 mmHg)]; ^{1}H NMR δ 3.75 (d, J = 11.1 Hz, 3H), 7.30−7.80 (m, 10H); ^{31}P NMR δ 33.7.

Data for **2** (R = Et): colorless oil; bp 170−172 °C (1.5 mmHg) [lit.[17] bp 172 °C (1.5 mmHg)]; ^{1}H NMR δ 1.37 (t, J = 7.0 Hz, 3H), 4.11 (dt, $J_{PH} = J_{HH}$ = 7.0 Hz, 2H), 7.30−7.96 (m, 10H); ^{31}P NMR δ 31.9.

Data for **3** (R = *i*-Pr): white solid; mp 97−99 °C (lit.[16] mp 97−99 °C); ^{1}H NMR δ 1.35 (d, J = 6.2 Hz, 6H), 4.60−4.70 (m, 1H), 7.28−7.90 (m, 10H); ^{31}P NMR δ 30.9.

Data for **4** (R = *t*-Bu): white solid mp 110−112 °C (lit.[16] mp 111−112 °C); ^{1}H NMR δ 1.53 (s, 9H), 4.60−4.70 (m, 1H), 7.42−7.81 (m, 10H); ^{31}P NMR δ 26.3.

Kinetic Measurements. In a typical procedure, a standardized solution (15 mL) of substrate **1**−**4** (0.012−0.07 M) was added to a standardized solution (15 mL) of complexed MI or MI$_2$ (0.004−0.03 M) in a 50 mL flask thermostated at 60 ± 0.1 °C. Samples (2−10 mL), withdrawn periodically, were quenched in ice-cold MeOH (50 mL), and the unreacted nucleophile I$^-$ was potentiometrically titrated with 0.01 N AgNO$_3$.

Alternatively, a standardized solution (10 mL) of substrate **1** (0.0030−0.04 M), tetradecane as internal standard (0.02 M), and anhydrous triethylamine (0.02 M) was added to a standardized solution (10 mL) of preformed complex or hexyl$_4$N$^+$I$^-$ (0.02 M). Samples (0.5−1 mL), withdrawn periodically, were quenched with an aqueous saturated solution of AgNO$_3$ (1 mL) and analyzed by GC. The mass balance was $\geq$97% in all cases.

The second-order rate constants were evaluated using a least-squares computer program from the eq $1/([B_0] - [A_0]) \ln ([B][A_0])/[A][B_0]) = kt$, where A = substrate and B = complexed iodide or hexyl$_4$N$^+$I$^-$ or vice versa. All rates involved at least eight samplings and gave correlation coefficients of 0.995 or better.

The solutions of preformed complexes of **5**−**7** were prepared by magnetically stirring a standardized solution (30 mL) of ligand in the organic solvent (chlorobenzene, 1,2-dichlorobenzene or toluene) (0.01−0.03 M) with the appropriate quantity of salt MI or MI$_2$ (0.2−1.3 mol per mol of ligand) as a solid phase, in a flask thermostated at 60 ± 0.1 °C. The heterogeneous system was stirred for 1−3 h and then kept without stirring for an additional 10 min to allow good separation of the two phases. Aliquots (5−8 mL) of the organic phase were centrifuged and samples (2−5 mL) were withdrawn and titrated with 0.01 N AgNO$_3$.

Acknowledgment. We gratefully acknowledge the support of this research by CNR and MURST.

JO0056388

---

[12] Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed.; Verlag-Chemie: Weinheim, 1988.

[13] Maia, A. *Pure Appl. Chem.* **1995**, *67*, 697.

[14] Landini, D.; Maia, A.; Penso, M. *Comprehensive Supramolecular Chemistry*; Lehn, J. M., Ed.; Pergamon Press: Oxford, 1996; Vol. 1, Chapter 11, pp 417−464.

[15] Modro, A. M.; Modro, T. A. *Can. J. Chem.* **1993**, *71*, 469.

[16] Berlin, K. D.; Austin, T. H.; Nagabhushanam, M. *J. Org. Chem.* **1965**, *30*, 1267.

[17] Allen, D. W.; Hutley, B. G.; Meller, M. T. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1705.