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New Synthetic Routes to Cationic Rhenium Tricarbonyl Bipyridine Complexes with Labile Ligands

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Triflate abstraction from the complex [Re(OTf)(CO)$_3$(bipy)] (**1**) using the salt NaBAr′$_4$ (Ar′ = 3,5-bis(trifluoromethyl)-phenyl) in dichloromethane solution in the presence of L = PPh_3, NCMe, NCPh, imines, ketones, Et_2O, THF, MeOH, and MeI affords cationic complexes [Re(L)(CO)$_3$(bipy)]$^+$ as their BAr′$_4^-$ salts. The new complexes have been characterized spectroscopically and, for [Re(η^1-O=C(Me)R)(CO)$_3$(bipy)]BAr′$_4$ (R = CH_3, **6a**; R = Ph, **6b**), and [Re(THF)(CO)$_3$(bipy)]BAr′$_4$ (**9**), also by single-crystal X-ray diffraction. Compared with conventional methodologies, the route reported here allows the coordination of a broader range of weakly coordinating ligands and requires considerably milder conditions. On the other hand, the reactions of lithium acetylides with [Re(THF)(CO)$_3$(bipy)]-BAr′$_4$ (**9**) can be used for the high-yield syntheses of rhenium alkynyls [Re(C≡CR)(CO)$_3$(bipy)] (R = Ph, **12**; R = $SiMe_3$, **13**). Complex **9** was found to catalyze the aziridination of benzylideneaniline with ethyl diazoacetate.

Introduction

Rhenium tricarbonyl diimine complexes have been the subject of much attention, mainly because of their photophysical and photochemical properties[1] and their use in CO_2 activation[2] and in supramolecular chemistry.[3] The starting materials [ReX(CO)$_3$(N−N)] (X = Cl, Br) are easily prepared by the reactions of diimines with [ReX(CO)$_5$] complexes, in turn obtained by direct [$Re_2(CO)_{10}$] oxidation with the halogen.[4] However, the functionalization of [ReX-(CO)$_3$(bipy)] compounds may present difficulties. For instance, the reaction of these halocomplexes with lithium acetylides is not a good method to prepare alkynyl complexes which have been targeted by Yam because of their interesting luminiscence behavior.[5] Similar difficulties are encountered with other anionic nucleophiles.[6] On the other hand, the

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substitution of halide by neutral ligands to give cationic complexes has been effected via the more labile triflato complexes. Even in this way, triflate substitution requires forcing conditions. Thus, the preparation of $[Re(PPh_3)(CO)_3(bipy)]OTf$ from $[Re(OTf)(CO)_3(bipy)]$ needed the presence of 100 equiv of the phosphine.[2j] Substitution of nitrile ligands, which are typically employed as labile neutral leaving groups, is also slow in these rhenium compounds: nitrile substitution in $[Re(NCMe)(CO)_3(bdz)]^+$ (bdz = bidiazine)[7] required 10 equiv of PPh_3 and 2 h in refluxing THF. This obviously imposes a serious limitation with regard to the synthesis of complexes with ligands more labile than nitriles. It would be desirable to develop a method for the functionalization of $[ReX(CO)_3(N-N)]$ complexes without harsh conditions or large excesses of ligands.

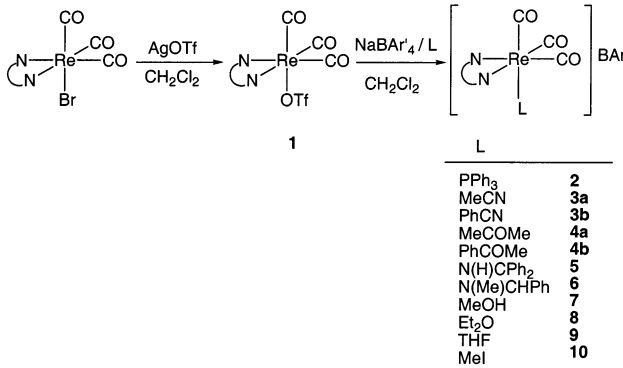
Bergman[8] and Caulton[9] used the reaction of neutral triflato complexes with the salt $NaBAr'_4$[10] (Ar′ = 3,5-bis(trifluoromethyl)phenyl) in CH_2Cl_2 to generate cationic complexes having labile ligands. The reaction takes advantage of the low solubility of sodium triflate in CH_2Cl_2 and affords salts of the cationic complexes with the low-coordinating, inert BAr'_4 counterion.[11] Here, we report the application of this method to the preparation of cationic labile complexes of the fragment $\{Re(CO)_3(bipy)\}$ and the use of one of these cationic complexes in the synthesis of alkynyls and in the catalytic synthesis of aziridines.

Results and Discussion

The addition of a slight excess of either triphenylphosphine, acetonitrile, or benzonitrile to a solution of $[Re(OTf)(CO)_3(bipy)]$ (**1**)[12] in dichloromethane at room temperature did not cause triflate dissociation. Thus, the spectroscopic (IR and NMR) observation of the resulting solution over 24 h only showed the signals of the reactants. Even when the mixtures were refluxed in toluene for 5 h, no reaction was observed.

The addition of 1 equiv of the salt $NaBAr'_4$ (Ar′ = 3,5-bis(trifluoromethyl)phenyl)[10] to these solutions at room temperature made them become inmediately cloudy because of the formation of sodium triflate, insoluble in CH_2Cl_2. The IR of the solutions showed that the bands of **1** were replaced by new ones at higher wavenumbers (see Experimental Section), as expected for the formation of cationic complexes. ν_{CO} patterns corresponding to *fac*-tricarbonyl complexes were observed. The ^1H NMR spectra, with four multiplets in the bipy region, reflecting the existence of a mirror plane, showed that a single product was obtained in each case. IR monitoring showed that these reactions reached completion in about 10 min. Spectroscopic data, given in the Experimental Section, indicate that the products are $[Re(L)(CO)_3(bipy)]BAr'_4$ (L = PPh_3,[2c] **2**; MeCN,[13] **3a**; PhCN, **3b**) complexes, as depicted in Scheme 1.

Scheme 1



The addition of the equimolar amount of $NaBAr'_4$ to a solution of $[Re(OTf)(CO)_3(bipy)]$ (**1**)[10] in CH_2Cl_2 resulted in cloudiness and a shift to higher wavenumbers of the solution ν_{CO} IR bands. This is consistent with generation of a cationic dichloromethane adduct. However, all our attempts to isolate or characterize this species beyond the IR spectrum failed. Nevertheless, its solution reacted instantaneously with equimolar amounts of PPh_3, MeCN, or PhCN to produce the complexes **2**, **3a**, and **3b**, respectively.

These results encouraged us to apply the synthetic method outlined here to the preparation of new cationic complexes $[Re(L)(CO)_3(bipy)]BAr'_4$. Thus, when a mixture of **1**, benzophenone imine, and $NaBAr'_4$ was dissolved in CH_2Cl_2, a reaction immediately ensued, from which a crystalline product with data consistent with $[Re(HN{=}CPh_2)(CO)_3(bipy)]BAr'_4$ (**4**) composition was isolated (see Scheme 1 and Experimental Section). In the ^{13}C NMR of **4**, a broad, weak signal at 179.33 ppm was attributed to the C=N carbon of the imine ligand. A downfield shift upon coordination (the corresponding signal of free benzophenone imine appears at 178.21 ppm) was previously noted for imine carbons.[14] The four bipy signals in the ^1H NMR of **4** are consistent with either the presence of a mirror plane in a static molecule (the imine would be contained in the plane of the $\{Re(CO)_3(bipy)\}$ fragment) or with free rotation around the Re−N(imine) bond.

We have recently found that stoichiometric amounts of arylamines effect the substitution of triflate in complex **1** under mild conditions.[15] This difference with the behavior of PPh_3 or NCR (see previous description) can be attributed to the higher nucleophilicity of amines. We wished to find whether imines, less nucleophilic, display a similar reactivity. Complexes of monodentate imines are relatively rare, a fact

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(11) Coordination, hydrolysis, and fluoride transfer have been noted for more conventional anions, such as tetrafluoroborate or hexafluorophosphate.
(12) Guerrero, J.; Pino, O. E.; Wolcan, E.; Feliz, M. R.; Ferraudi, G.; Moya, S. A. *Organometallics* **2001**, *20*, 2842−2853.
(13) This complex has been previously prepared by reaction of complex $[ReCl(CO)_3(bipy)]$ and $AgPF_6$ in MeCN, refluxed for 8 h. See ref 7.
(14) (a) Knight, D. A.; Dewey, M. A.; Stark, G. A.; Bennett, B. K.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1993**, *12*, 4523−4534. (b) Gunnoe, T. B.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 6916−6923.
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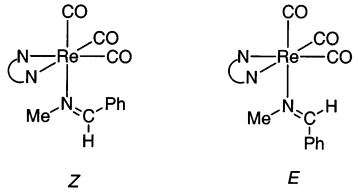
Chart 1



that has been attributed to the low basicity of imines and their vulnerability to nucleophilic attack.[16] A mixture of **1** and 3 equiv of benzophenone imine showed (^{1}H NMR monitoring) a complete transformation of **1** into the complex [Re(HN=CPh$_2$)(CO)$_3$(bipy)]OTf in 15 h.

The reaction of [Re(OTf)(CO)$_3$(bipy)] (**1**), NaBAr′$_4$, and the *N*-methylimine MeN=CHPh in CH_2Cl_2 led to the formation of the compound [Re(MeN=CHPh)(CO)$_3$(bipy)]-BAr′$_4$ (**5**) which was isolated as a microcrystalline solid.[17] Its ^{1}H and ^{13}C NMR spectra showed the presence of two species in an approximate 2:1 ratio. In addition to the bipy and aryl signals, the ^{1}H NMR showed doublets at 3.49 (major) and 3.40 (minor) ppm, with similar coupling constants (of about 1.5 Hz), assignable to the CH_3 groups. The ^{13}C NMR spectrum showed signals corresponding to the imine carbons at 178.55 (major) and 175.72 (minor) ppm. This set of data is consistent with the existence of the two *Z* and *E* isomers of **5** (see Chart 1) in solution, and it can be assumed that the major species corresponds to the *E* diasteromer because, having the bulkier substituents in distant positions, it must be the most stable.

To evaluate the scope of the synthetic method, we aimed to prepare complexes of ketones, which are very labile ligands for organometallic fragments.[18] The reaction of **1**, NaBAr′$_4$, and acetone or acetophenone afforded the adducts [Re(η^1-O=C(Me)R)(CO)$_3$(bipy)]BAr′$_4$ (R = CH_3, **6a**; R = Ph, **6b**, see Scheme 1), which were crystallized by slow diffusion of hexanes into their CH_2Cl_2 solutions. Both compounds were characterized by IR and NMR (^{1}H and ^{13}C) spectroscopy and by X-ray diffraction (Figure 1 and Table 1 for complex **6a**, and Figure 2 and Table 2 for complex **6b**). The two compounds showed IR spectra with bands at 1621 (**6a**) and 1661 (**6b**) cm^{-1}, corresponding to the C=O stretchings of the ketone ligands. These values differ little from those of the free ketones (1712 cm^{-1} for acetone and 1684 cm^{-1} for acetophenone). The ^{13}C NMR chemical shifts of the ketone carbons are also slightly shifted with respect to the free ketones (228.38 (**6a**) and 214.97 (**6b**) ppm).[19]

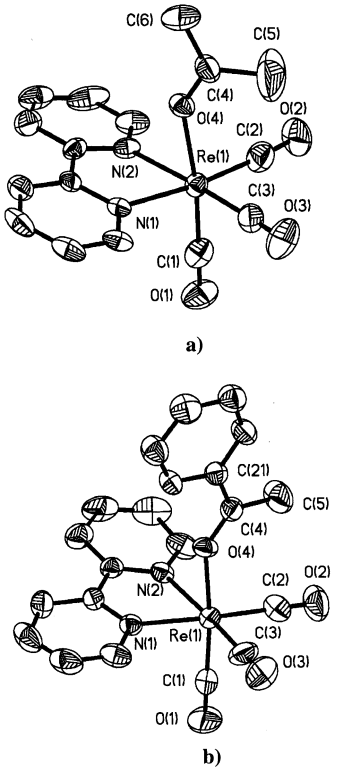


Figure 1. Thermal ellipsoid (30%) plots of **6a** (a) and **6b** (b).

Table 1. Selected Bond Distances and Angles for Complexes **6a**, **6b**, and **9**

	6a	**6b**	**9**
Re(1)−C(1)	1.911(13)	1.913(13)	1.818(13)
Re(1)−C(2)	1.914(12)	1.933(13)	1.919(12)
Re(1)−C(3)	1.931(13)	1.930(13)	1.921(11)
Re(1)−N(1)	2.154(6)	2.153(7)	2.162(6)
Re(1)−N(2)	2.143(6)	2.174(7)	2.166(6)
Re(1)−O(4)	2.183(6)	2.167(6)	2.228(5)
C(3)−O(3)	1.124(12)	1.137(13)	1.175(12)
C(1)−O(1)	1.147(12)	1.139(13)	1.161(12)
C(2)−O(2)	1.138(13)	1.144(13)	1.126(10)
O(4)−C(4)	1.181(11)	1.218(10)	
C(1)−Re(1)−C(2)	87.9(5)	86.5(5)	89.1(4)
C(3)−Re(1)−C(2)	86.4(5)	88.1(5)	88.7(4)
C(1)−Re(1)−C(3)	89.5(5)	89.5(4)	88.0(4)
C(2)−Re(1)−N(1)	173.3(4)	174.1(4)	171.6(3)
C(1)−Re(1)−N(1)	95.8(4)	92.9(4)	95.7(3)
C(3)−Re(1)−N(1)	98.2(3)	97.8(5)	98.3(3)
C(2)−Re(1)−N(2)	99.8(4)	100.0(4)	98.4(3)
C(3)−Re(1)−N(2)	172.1(4)	170.2(4)	172.9(3)
N(2)−Re(1)−N(1)	74.4(2)	74.2(3)	74.6(2)
C(1)−Re(1)−N(2)	94.0(4)	96.3(4)	92.8(3)
C(2)−Re(1)−O(4)	95.6(4)	99.5(6)	91.5(3)
C(1)−Re(1)−O(4)	172.5(4)	174.0(4)	179.4(3)
C(3)−Re(1)−O(4)	97.4(3)	90.7(4)	92.2(3)
N(1)−Re(1)−O(4)	80.1(2)	81.2(2)	83.7(2)
N(2)−Re(1)−O(4)	78.9(2)	82.6(2)	87.0(2)
C(4)−O(4)−Re(1)	140.6(7)	137.6(6)	
O(4)−C(4)−C(5)	120.5(12)	121.8(9)	

These data indicate a σ-coordination (larger differences to lower values with respect to the free ketones are observed both for ν_{CO} values and for ^{13}C chemical shifts in π-coordinated ketones).[20] The ^{1}H NMR of the acetone complex **6a** shows a single signal for the two methyl groups, consistent

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(17) We have found that the triflato complex **1** did not react with MeN=CHPh (3 equiv of imine, refluxing toluene, 6 h). It was previously noted by Gladysz (see ref 14a) that the coordination of this imine required vigorous conditions, because of the decreased nucleophilicity resulting from the methyl substitution at nitrogen. In our case, the difference between the reaction with or without NaBAr′$_4$ illustrates the utility of this salt as a triflate abstractor.

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(19) The ^{13}C NMR chemical shifts of the ketone carbons are 206.71 and 198.08 ppm for free acetone and free acetophenone, respectively.

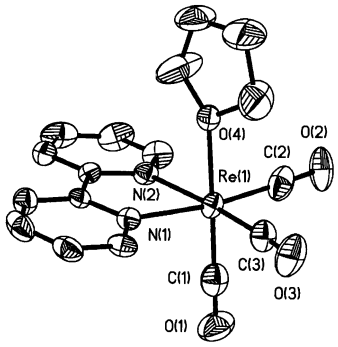

Figure 2. Thermal ellipsoid (30%) plot of **9**.

Table 2. Crystal Data and Refinement Details for Complexes **6a**, **6b**, and **9**

	6a	**6b**	**9**
formula	$C_{48}H_{26}BF_{24}N_2O_4Re$	$C_{53}H_{28}BF_{24}N_2O_4Re$	$C_{49}H_{28}BF_{24}N_2O_4Re$
fw	1347.72	1409.78	1361.74
cryst syst	orthorhombic[a]	orthorhombic	orthorhombic
space group	*Pna*2(1)	*Pna*2(1)	*Pna*2(1)
a, Å	16.820(4)	17.181(6)	16.849(4)
b, Å	16.663(4)	15.957(6)	16.734(4)
c, Å	18.351(5)	20.129(7)	18.467(5)
α, deg	90	90	90
β, deg	90	90	90
γ, deg	90	90	90
V, Å^3	5143(2)	5518(3)	5207(2)
Z	4	4	4
T, K	293(2)	293(2)	299(2)
D_c, g cm^{-3}	1.741	1.697	1.737
F(000)	2624	2572	2656
λ(Mo Kα), Å	0.71073	0.71073	0.71073
cryst size, mm^3	0.1 × 0.15 × 0.3	0.13 × 0.15 × 0.3	0.08 × 0.11 × 0.11
μ, mm^{-1}	2.495	2.330	2.466
scan range, deg	$1.65 \le \theta \le 23.37$	$1.63 \le \theta \le 23.28$	$1.64 \le \theta \le 23.29$
no. reflns measured	32465	34647	32702
no. independent reflns	7439	7941	7496
data/restraints/params	7439/1/723	7941/1/767	7496/1/731
GOF on F^2	1.019	1.020	1.004
R1/wR2 [$I > 2\sigma(I)$]	0.0384/0.0884	0.0405/0.1007	0.0366/0.0819
R1/wR2 (all data)	0.0487/0.0951	0.0529/0.1090	0.0508/0.0863

[a] In the structure of **6a**, the close proximity of the values of the unit cell parameters *a* and *b* suggested the possibility of a tetragonal cell. However, the attempt to merge the reflections in tetragonal symmetry gave $R_{int} > 0.5$ (cf. R_{int} 0.0462 for the orthorhombic cell). Therefore, the solution and refinement were carried out in the orthorhombic space group *Pna*2(1) with successful results (see data in Table 1).

with a rapid dissociation−recoordination process of the ketone. For complex **6b**, only one methyl signal is seen the ^{1}H NMR, and only one methyl group and one phenyl group appear in ^{13}C NMR. This can be attributed to the lability of the ketone. Although for the asymmetric ketone it could also be due to the large preponderance of one of the geometric isomers (in the solid state the disposition of the Ph and {Re(CO)$_3$(bipy)} groups is *trans* with respect to the double bond, presumably to minimize steric interaction between these bulkier substituents), the occurrence of a similar lability for the acetone complex **6a** makes us favor the former hypothesis.

The only Re(I) cationic complexes with ketone ligands previously characterized by X-ray diffraction are of the kind [ReCp(η^1-O=C(Me)R)(NO)(PPh$_3$)]$^+$.[18a] These species show Re−O distances shorter (R = Me, 2.099(5) Å; R = Ph, 2.080(5) Å) than in **6a** (2.183(6) Å) and **6b** (2.167(6) Å). This can be due, at least in part, to the different geometry; thus, unlike the cyclopentadienyl compounds, [Re(η^1-O=C(Me)R)(CO)$_3$(bipy)]BAr′$_4$ complexes are octahedral and have the ketone ligand *trans* to a CO ligand, with a strong *trans* influence.[21]

Alcohols and ethers, which are usually even poorer ligands than ketones,[22] can also be coordinated to the cationic fragment {Re(CO)$_3$(bipy)}$^+$ employing the method outlined previously. Thus, the reactions of **1**, NaBAr′$_4$, and methanol, diethyl ether, or tetrahydrofuran (THF) in CH_2Cl_2 afforded the compounds [Re(MeOH)(CO)$_3$(bipy)]BAr′$_4$ (**7**), [Re(Et$_2$O)(CO)$_3$(bipy)]BAr′$_4$ (**8**), and [Re(THF)(CO)$_3$(bipy)]BAr′$_4$ (**9**), respectively (Scheme 1). These compounds were characterized spectroscopically (see Experimental Section) and, in the case of **9**, by X-ray diffraction (Figure 2 and Table 1).

The Re−O distance (2.228(5) Å) in **9** is nearly identical to that found for the complex [{Re(CO)$_3$(THF)}$_2$(μ-Cl)$_2$],[23] which also features an octahedral geometry around each rhenium, and a CO *trans* to the THF ligand.

Equimolar amounts of [Re(OTf)(CO)$_3$(bipy)] and NaBAr′$_4$ were dissolved in CD_2Cl_2, and after filtration to remove NaOTf, 6 equiv of Et$_2$O was added. The ^{1}H NMR monitoring of the resulting solution showed the complete formation of [Re(Et$_2$O)(CO)$_3$(bipy)]BAr′$_4$ (**8**) in 1 h. The Et$_2$O ligand of **8** displayed signals at 3.66 (quartet) and 1.05 (triplet) ppm. The presence of separate signals for free and coordinated Et$_2$O indicates that a fast exchange is not taking place.[24]

As found for the ether complex **8**, also the complex [Re(MeOH)(CO)$_3$(bipy)]BAr′$_4$ (**7**) crystallizes with one molecule of methanol, and also in this case, the free coordinated methanol gives separated signals in the ^{1}H NMR spectrum (see Experimental Section), indicating the absence of a fast exchange process.

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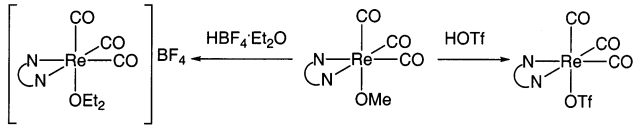
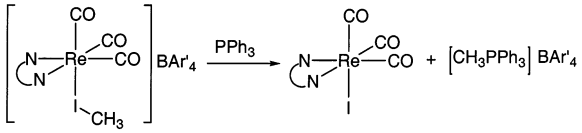
(24) In contrast with the stability of [Re(Et$_2$O)(CO)$_3$(bipy)]BAr′$_4$ (**8**) in dichloromethane solution, Gladysz found that the reaction of [ReCp(CH$_3$)(NO)(PPh$_3$)] with HBF$_4$·Et$_2$O in dichloromethane in the presence of 20−25 equiv of Et$_2$O afforded [ReCp(ClCH$_2$Cl)(NO)(PPh$_3$)]BF$_4$ as a single product: Agbossou, S. K.; Fernández, J. M.; Gladysz, J. A. *Inorg. Chem.* **1990**, *29*, 476−480. An analogous preference for CH_2Cl_2 over Et$_2$O was found by Kubas for the complexes of the fragment {PtH(P^{i}Pr$_3$)$_2$}$^+$: Huhmann-Vincent, J.; Scott, B. L.; Kubas, G. J. *Inorg. Chem.* **1999**, *38*, 115−124. The difference between **8** and these compounds can be attributed to the presence of bulky phosphine ligands in the latter, a feature that should disfavor the coordination of the more sterically demanding molecule of Et$_2$O. The lower steric profile of the {Re(CO)$_3$(bipy)}$^+$ fragment (the bipy ligand is planar and lacks bulky substituents), on the other hand, favors the coordination of the stronger donor Et$_2$O against dichloromethane.

Scheme 2



Scheme 3

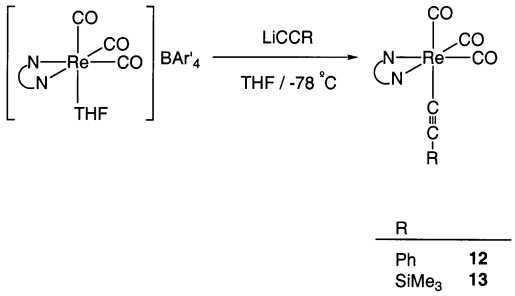


Protonation of methoxo ligands has been used to generate methanol complexes.[25] We investigated the protonation of the complex $[Re(OMe)(CO)_3(bipy)]$[26] using the commercially available acids HOTf or $HBF_4{\cdot}Et_2O$ as an alternative synthesis of the cationic complex present in **7**. However, the triflato complex $[Re(OTf)(CO)_3(bipy)]$ (**1**) and the ether adduct $[Re(OEt_2)(CO)_3(bipy)]BF_4$ (see Experimental Section), respectively, were obtained instead (see Scheme 2).

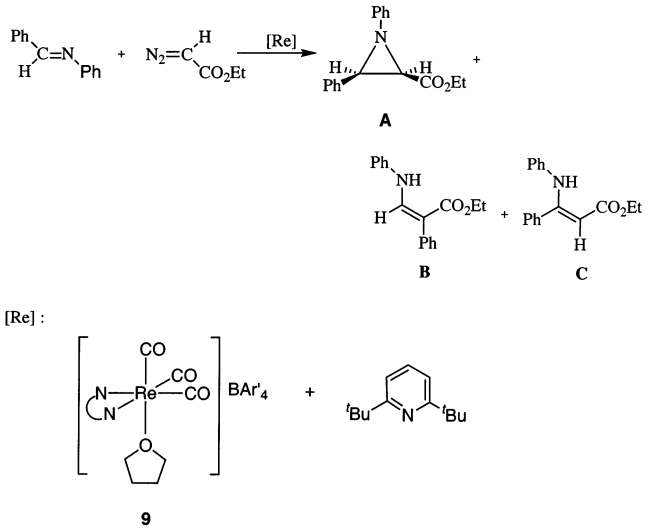
As mentioned previously, the dichloromethane adduct proposed as an intermediate in the described triflate substitution eluded our isolation attempts. Given that alkyl iodides are known to be better ligands than chlorides,[27] we thought that an iodoalkane adduct could be stable enough to permit isolation. As a matter of fact, the reaction of **1** and $NaBAr'_4$ in neat iodomethane yielded the compound $[Re(IMe)(CO)_3(bipy)]BAr'_4$ (**10**), which could be crystallized and characterized by spectroscopy and C, H, N analysis (see Experimental Section). In contrast with the reaction of PPh_3 and the in situ generated $[Re(ClCH_2Cl)(CO)_3(bipy)]BAr'_4$ species, which led to phosphine coordination, the reaction of PPh_3 with **10** afforded the complex $[ReI(CO)_3(bipy)]$, as a result of phosphine attack on the methyl group (see Scheme 3). This difference is due to the higher electrophilicity and better ligating properties of the iodoalkane. The activation of haloalkanes toward nucleophilic attack by coordination to cationic metal centers has been previously found.[28]

When the complex $[ReI(CO)_3(bipy)]$ was allowed to react with methyl triflate, $[Re(OTf)(CO)_3(bipy)]$ (**1**) was obtained as a single product. This indicates that the iodo ligand is methylated (this kind of reaction has been used for synthesis of iodoalkane adducts)[29] and that the triflate anion substituted the resulting CH_3I ligand. This contrasts with the isolability of $[Re(IMe)(CO)_3(bipy)]BAr'_4$ (**10**) and, once again, shows the importance of using low coordinating counterions in the synthesis of labile cationic complexes.[30]

Scheme 4



Scheme 5



The lability of the cationic compounds described here can be taken advantage of to prepare neutral $[ReX(CO)_3(bipy)]$ complexes. Thus, the reaction of equimolar amounts of lithium acetylides LiC≡CR (R = Ph, $SiMe_3$) with $[Re(THF)(CO)_3(bipy)]BAr'_4$ (**9**) at −78 °C instantaneously afforded the alkynyls $[Re(C{\equiv}CPh)(CO)_3(bipy)]$ (**12**) and $[Re(C{\equiv}CSiMe_3)(CO)_3(bipy)]$ (**13**), respectively (see Scheme 4), which could be isolated as pure materials after a simple workup procedure (see Experimental Section). It should be noted that the synthesis of these alkynyls by the reaction of $[ReCl(CO)_3(bipy)]$ with lithium acetylides fails to yield the desired alkynyls.[5]

We mentioned previously that the labile cationic complexes reported here are strong Lewis acids. This, and the fact that both the BAr'_4 anion and the $\{Re(CO)_3(bipy)\}$ fragment are usually robust (neither the carbonyl nor the bipy ligands dissociate facilely), led us to study the catalytic activity of these compounds in the synthesis of aziridines from ethyldiazoacetate (EDA) and benzylideneaniline. Thus, when 1% of **9** (along with 2,6-di-*tert*-butylpyridine as acid scavenger) was added to an equimolar mixture of EDA and the imine in CH_2Cl_2, full conversion to a mixture of the *cis*-(carboxyethyl)-1,3-diphenylaziridine **A** (see Scheme 5) and the enamines **B** and **C** (aziridine/enamines ratio = 5:2) was observed in 12 h at room temperature. The absence of diethyl maleate/fumarate in the crude mixtures obtained as products indicates that the metal complex acts as a Lewis acid to which the imine coordinates rather than as a carbene transfer reagent.[31]

(25) See for instance: Caldarelli, J. L.; Wagner, L.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1994**, *116*, 2878−2888.
(26) (a) Gibson, D. H.; Sleaad, B. A.; Yin, X.; Vij, A. *Organometallics* **1998**, *17*, 2689−2691. (b) Hevia, E.; Pérez, J.; Riera, L.; Riera, V.; Miguel, D. *Organometallics*, **2002**, *21*, 1750−1752.
(27) Kulawiec, R. J.; Crabtree, R. H. *Coord. Chem. Rev.* **1990**, *89*, 89−115.
(28) (a) Czech, P. T.; Gladysz, J. A.; Fenske, R. F. *Organometallics* **1989**, *8*, 1806−1810. (b) Winter, C. H.; Veal, W. V.; Garner, C. M.; Arif, M. A.; Gladysz, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 4766−4776. (c) Igau, A.; Gladysz, J. A. *Organometallics* **1990**, *10*, 2327−2334.
(29) Kulawiec, R. J.; Crabtree, R. H. *Organometallics* **1988**, *7*, 1891−1893.
(30) Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927−942.

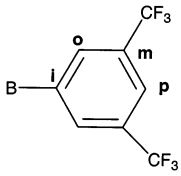


Figure 3. Hydrogen/carbon labeling atoms scheme of the BAr'_4 anion.

Experimental Section

General Procedures. General procedures have been given elsewhere.[15] [$ReBr(CO)_3$(bipy)] was prepared in quantitative yield by refluxing the equimolar amount of [$ReBr(CO)_5$][4] and bipy in toluene for 4 h. [$Re(OTf)(CO)_3$(bipy)] (**1**) was prepared by the reaction of equimolar amounts of [$ReBr(CO)_3$(bipy)] with AgOTf in CH_2Cl_2 in the dark, followed by filtration through diatomaceous earth to remove AgBr. ^{13}C NMR signals of the BAr'_4 anion are almost identical in all complexes and are given only for **2** (Figure 3).

Crystal Structure Determination for Compounds 6a, 6b, and 9. A Bruker AXS SMART 1000 diffractometer with CCD area detector was used. Raw frame data were integrated with the SAINT[32] program. The structure was solved by direct methods with SHELXTL.[33] A semiempirical absorption correction was applied with the program SADABS.[34] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined as riding atoms, with a common thermal parameter. All calculations and graphics were made with SHELXTL.

Preparation of [Re(L)$(CO)_3$(bipy)]BAr'_4 (2−10). General Description. Dichloromethane (15 mL) was added to a mixture of [$Re(OTf)(CO)_3$(bipy)] (**1**) (0.050 g, 0.036 mmol) and $NaBAr'_4$ (0.077 g, 0.036 mmol).[35] The ligand L was added,[36] and the resulting solution was stirred 1 h and then filtered with a cannula tipped with filter paper. Diffusion of hexanes into these solutions[37] afforded crystals of the [Re(L)$(CO)_3$(bipy)]BAr'_4 complexes (**2**−**10**). All the new complexes are yellow. IR spectra are given in CH_2Cl_2, and NMR spectra in CD_2Cl_2.

[Re(PPh_3)$(CO)_3$(bipy)]BAr'_4 (2). Yield: 0.042 g, 75%. IR: 2041, 1957, 1928. ^1H NMR: 8.57 [m, 2H, bipy], 7.99 [m, 4H, bipy], 7.77 [m, 10H, 8H H−C_o BAr'_4 and 2H bipy], 7.58 [m, 4H H−C_p BAr'_4], 7.29−7.13 [m, 15H, PPh_3]. $^{13}C\{^1H\}$ NMR: 195.05 [2CO], 186.70 [d (58.14), CO], 162.16 [q (49.79), C_I BAr'_4], 155.37, 154.03, 140.17 [bipy], 135.19 [s, C_o BAr'_4], 134.78 [d (10.7), PPh_3], 133.25 [d (54.7), PPh_3], 130.95 [d (2.8), PPh_3], 129.49 [bipy], 128.68 [d (10.4), PPh_3], 128.18 [q (31.1), C_m BAr'_4], 124.94 [q (272.59), CF_3], 123.91 [bipy], 117.87 [C_p BAr'_4]. Anal. Calcd for $C_{63}H_{35}BF_{24}N_2O_3PRe$: C, 48.75; H, 2.27; N, 1.80. Found: C, 48.87; H, 2.34; N, 1.68.

[Re(MeCN)$(CO)_3$(bipy)]BAr'_4 (3a). Yield: 0.039 g, 82%. IR: 2044, 1943. ^1H NMR: 9.01 [m, 2H, bipy], 8.20 [m, 4H, bipy], 7.74 [m, 10H, 8H H−C_o BAr'_4 and 2H bipy], 7.57 [m, 4H H−C_p BAr'_4], 2.09 [s, 3H, CH_3]. $^{13}C\{^1H\}$ NMR: 193.32 [2CO], 189.46 [CO], 156.04, 154.18. 141.24, 128.80, 124.20 [bipy], 121.77 [CH_3CN], 3.78 [CH_3CN]. Anal. Calcd for $C_{46}H_{23}BF_{24}N_3O_3Re$: C, 41.89; H, 1.75; N, 3.18. Found: C, 41.67; H, 1.62; N, 3.28.

[Re(PhCN)$(CO)_3$(bipy)]BAr'_4 (3b). Yield: 0.040 g, 80%. IR: 2044, 1946. ^1H NMR: 9.10 [m, 2H, bipy], 8.20 [m, 4H, bipy], 7.74 [m, 8H H−C_o BAr'_4], 7.69 [m, 2H, bipy], 7.55 [m, 4H H−C_p BAr'_4], 7.42 [m, 5H, Ph]. $^{13}C\{^1H\}$ NMR: 193.30 [2CO], 189.83 [CO], 156.09, 154.28. 141.31 [bipy], 136.10, 133.54, 129.96 [Ph], 128.87 [bipy], 122.53 [Ph*C*N], 123.16 [bipy], 107.97 [Ph]. Anal. Calcd for $C_{52}H_{25}BF_{24}N_3O_3Re$: C, 44.84; H, 1.80; N, 3.01. Found: C, 44.71; H, 1.90; N, 3.18.

[Re(N(H)CPh_2)$(CO)_3$(bipy)]BAr'_4 (4). Yield: 0.041 g, 78%. IR: 2034, 1930. ^1H NMR: 9.03 [m, 3H, 2H bipy and 1H N*H*], 8.24 [m, 4H, bipy], 7.74 [m, 10H, 8H H−C_o BAr'_4 and 2H bipy], 7.57 [m, 4H H−C_p BAr'_4], 7.53 [m, 6H, 2Ph], 6.28 [m, 4H, 2Ph]. $^{13}C\{^1H\}$ NMR: 194.90 [2CO], 190.07 [CO], 188.42 [*C*═*N*], 155.58, 153.92. 141.12 [bipy], 137.00, 136.53, 134.28, 132.36. 130.37, 129.90 [2Ph], 129.64 [bipy], 124.59, 124.40 [2Ph], 123.99 [bipy]. Anal. Calcd for $C_{58}H_{31}BF_{24}N_3O_3Re$: C, 47.36; H, 2.12; N, 2.85. Found: C, 47.29; H, 2.25; N, 2.87.

[Re(N(Me)CHPh)$(CO)_3$(bipy)]BAr'_4 (5). Yield: 0.048 g, 84%. IR: 2038, 1929. ^1H NMR:[38] 8.66 [m, 2H bipy], 8.11 [m, 5H, 4H bipy and N═C*H*], 7.74 [m, 10H, 8H H−C_o BAr'_4 and 2H bipy], 7.57 [m, 4H H−C_p BAr'_4], 7.37 [m, 3H, Ph], 7.08 [m, 2H, Ph], 3.49 [d(1.5 Hz), 3H, CH_3]. $^{13}C\{^1H\}$ NMR: 195.40 [2CO], 189.83 [CO], 179.33 [*C*═N], 155.83, 153.97. 140.77 [bipy], 133.08, 131.76, [Ph], 129.01 [bipy], 128.31, 127.72 [Ph], 124.06 [bipy], 56.80 [CH_3]. Anal. Calcd for $C_{52}H_{29}BF_{24}N_3O_3Re$: C, 44.71; H, 2.09; N, 3.00. Found: C, 44.83; H, 2.15; N, 3.07.

[Re(MeCOMe)$(CO)_3$(bipy)]BAr'_4 (6a). Yield: 0.043 g, 88%. IR: 2040, 1934, 1621(*C*═*O*). ^1H NMR: 9.11 [m, 2H, bipy], 8.25 [m, 4H, bipy], 7.73 [m, 10H, 8H H−C_o BAr'_4 and 2H bipy], 7.54 [m, 4H H−C_p BAr'_4], 2.28 [s, 6H, CH_3]. $^{13}C\{^1H\}$ NMR: 228.38 [*C*═*O*], 195.30 [2CO], 190.98 [CO], 156.23, 153.99. 141.62, 129.11, 123.14 [bipy], 31.95 [CH_3]. Anal. Calcd for $C_{48}H_{26}BF_{24}N_2O_4Re$: C, 42.77; H, 1.94; N, 2.07. Found: C, 42.55; H, 1.98; N, 2.12.

[Re(MeCOPh)$(CO)_3$(bipy)]BAr'_4 (6b). Yield: 0.042 g, 84%. IR: 2040, 1934, 1661(*C*═*O*). ^1H NMR: 9.07 [m, 2H, bipy], 8.25 [m, 4H, bipy], 7.72 [m, 10H, 8H H−C_o BAr'_4 and 2H bipy], 7.54 [m, 4H H−C_p BAr'_4], 7.28 [m, 5H, Ph], 2.89 [s, 3H, CH_3]. $^{13}C\{^1H\}$ NMR: 214.97 [*C*═*O*], 196.85 [2CO], 192.67 [CO], 157.65, 155.56. 143.12 [bipy], 138.90, 136.04, 131.08, 129.85 [Ph], 129.49, 123.48 [bipy], 29.32 [CH_3]. Anal. Calcd for $C_{53}H_{28}BF_{24}N_2O_4Re$: C, 45.15; H, 2.00; N, 1.98. Found: C, 45.29; H, 2.15; N, 1.87.

[Re(MeOH)$(CO)_3$(bipy)]BAr'_4 (7). Yield: 0.030 g, 61%. IR: 2037, 1928. ^1H NMR: 9.08, 8.26 [m, 2H each, bipy], 7.73 [m, 10H, 8H H−C_o BAr'_4 and 2H bipy], 7.69 [m, 2H, bipy], 7.56 [m, 4H H−C_p BAr'_4], 5.81 [q (4.04 Hz), 1H, OH], 3.39 [d, 3H, CH_3], 3.24 [m, CH_3, free methanol]. $^{13}C\{^1H\}$ NMR: 195.49 [2CO], 189.92 [CO], 156.44, 154.11. 141.87, 128.87, 124.27 [bipy], 58.60 [CH_3], 51.37 [free methanol]. Anal. Calcd for $C_{47}H_{28}BF_{24}N_2O_5Re$: C, 41.82; H, 1.79; N, 2.07. Found: C, 41.75; H, 1.85; N, 2.16.

[Re(Et_2O)$(CO)_3$(bipy)]BAr'_4 (8). Yield: 0.045 g, 86%. IR: 2041, 1935. ^1H NMR: 9.05 [m, 2H, bipy], 8.25 [m, 4H, bipy], 7.74 [m, 10H, 8H H−C_o BAr'_4 and 2H bipy], 7.54 [m, 4H H−C_p BAr'_4], 3.66 [q (7.7 Hz), 4H, CH_2], 3.40 [q (7.3 Hz), 4H, CH_2, free ether], 1.05 [t (7.7), 6H, CH_3], 1.01 [t (7.3), 6H, CH_3, free ether]. $^{13}C\{^1H\}$ NMR: 195.55 [2CO], 189.86 [CO], 156.23, 154.08.

(31) (a) Casarrubios, L.; Pérez, J. A.; Brookhart, M.; Templeton, J. L. *J. Org. Chem.* **1996**, *61*, 8358−8360. (b) Morales, D.; Pérez, J.; Riera, L.; Riera, V.; Corzo-Suárez, R.; García-Granda, S.; Miguel, D. *Organometallics*, **2002**, *21*, 1540−1545.

(32) *SAINT+. SAX area detector integration program*, version 6.02; Bruker AXS, Inc.: Madison, WI, 1999.

(33) Sheldrick, G. M. *SHELXTL, An integrated system for solving, refining, and displaying crystal structures from diffraction data*; version 5.1; Bruker AXS, Inc.: Madison, WI, 1998.

(34) Sheldrick, G. M. *SADABS, Empirical Absorption Correction Program*; University of Göttingen: Göttingen, Germany, 1997.

(35) To prepare complex [Re(MeI)$(CO)_3$(bipy)]BAr'_4 (**10**), neat iodomethane was employed as solvent.

(36) Stoichiometric amounts of PPh_3 and nitriles, and 5 equiv of the remaining ligands used.

(37) The ether complex **8** was crystallized from hexane diffusion into a diethyl ether solution.

(38) NMR data are given for the major isomer.

141.82, 129.49, 124.24 [bipy], 67.75. [CH_2], 66.10 [CH_2, free ether], 17.16 [CH_3], 14.86 [CH_3, free ether]. Anal. Calcd for $C_{53}H_{40}BF_{24}N_2O_5Re$: C, 44.27; H, 2.80; N, 1.94. Found: C, 44.35; H, 2.85; N, 1.86.

[Re(THF)(CO)$_3$(bipy)]BAr′$_4$ (9). Yield: 0.039 g, 80%. IR: 2039, 1932. ^{1}H NMR: 9.11 [m, 2H, bipy], 8.25 [m, 4H, bipy], 7.73 [m, 10H, 8H H−C_o BAr′$_4$ and 2H bipy], 7.54 [m, 4H H−C_p BAr′$_4$], 3.51 [m, 4H, CH_2−O, THF], 1.71 [m, 4H, CH_2, THF]. ^{13}C-{^{1}H} NMR: 195.89 [2CO], 189.47 [CO], 156.20, 154.11. 142.02, 129.11, 123.14 [bipy], 77.41 [CH_2O, THF], 25.81 [CH_2, THF]. Anal. Calcd for $C_{49}H_{28}BF_{24}N_2O_4Re$: C, 43.21; H, 2.07; N, 2.05. Found: C, 43.34; H, 2.12; N, 2.11.

[Re(MeI)(CO)$_3$(bipy)]BAr′$_4$ (10). Yield: 0.035 g, 68%. IR: 2042, 1937. ^{1}H NMR: 9.07 [m, 2H, bipy], 8.25 [m, 4H, bipy], 7.72 [m, 10H, 8H H−C_o BAr′$_4$ and 2H bipy], 7.56 [m, 4H H−C_p BAr′$_4$], 2.26 [s, 3H, CH_3I]. ^{13}C{^{1}H} NMR: 195.01 [2CO], 189.45 [CO], 156.19, 154.33. 142.02, 129.01, 123.13 [bipy], 1.14 [CH_3I]. Anal. Calcd for $C_{46}H_{23}BF_{24}IN_2O_3Re$: C, 38.59; H, 1.65; N, 1.95. Found: C, 38.47; H, 1.72; N, 1.81.

Reaction of [Re(OMe)(CO)$_3$(bipy)] with HBF$_4$·Et$_2$O. [Re(OMe)(CO)$_3$(bipy)][26] (0.050 g, 0.109 mmol) was dissolved in CH_2Cl_2 (10 mL), and the solution was cooled at −78 °C. The stoichiometric amount of HBF_4·Et_2O (8 μL, 0.109 mmol) was added. The color of the solution changed from red to yellow. Volatiles were removed under vacuum, and the yellow solid was disolved in CH_2Cl_2 (5 mL). Slow diffusion of hexanes into this solution afforded crystals of [Re(OEt$_2$)(CO)$_3$(bipy)]BF_4·(**11**). Yield: 0.039 g, 62%. IR: 2041, 1935. ^{1}H NMR: 9.04, [m, 2H, bipy], 8.31 [m, 4H, bipy], 7.68 [m, 2H, bipy], 3.64 [q (7.7 Hz), 4H, CH_2], 1.10 [t (7.7), 6H, CH_3]. ^{19}F{^{1}H} NMR: −155.8. Anal. Calcd for $C_{17}H_{18}BF_4N_2O_4Re$: C, 34.76; H, 3.08; N, 4.76. Found: C, 34.67; H, 3.12; N, 4.80

Preparation of [Re(C≡CPh)(CO)$_3$(bipy)] (12). To a solution of phenylacetylene (4.5 μL, 0.040 mmol) in THF (10 mL) cooled to −78 °C was added ^{n}BuLi (25 μL of 1.6 M solution in hexane, 0.040 mmol), and the resulting solution of LiC≡CPh was transferred via cannula into a solution of [Re(THF)(CO)$_3$(bipy)]BAr′$_4$ (**9**) (0.054 g, 0.040 mmol) in THF (10 mL). The mixture was allowed to reach room temperature and stirred for 15 min. The resulting orange solution was evaporated in vacuo, and the residue was extracted with toluene cooled at 0 °C (3 × 10 mL) and filtered with a cannula tipped with filter paper. Pure **12** was obtained by slow diffusion of hexane into a THF solution. Yield: 0.014 g, 68%. IR (THF): 2096 ($\nu_{C\equiv C}$); 2006, 1902 (ν_{CO}). ^{1}H NMR: 9.06, 8.21, 7.81, 7.52 [m, 2H each, bipy], 6.96 [m, 3H, Ph], 6.84 [m, 2H, Ph]. ^{13}C{^{1}H} NMR: 199.03 [2CO], 192.03 [CO], 156.01, 153.41 [bipy], 148.75 [Ph], 138.81 [bipy], 131.51 [Ph], 128.04 [bipy], 127.20, 125.29 [Ph], 123.39 [bipy], 117.81, 105.80 [C≡CPh]. Anal. Calcd for $C_{21}H_{13}N_2O_3Re$: C, 47.81; H, 2.48; N, 5.31. Found: C, 47.79; H, 2.52; N, 5.51.

Preparation of [Re(C≡CSiMe$_3$)(CO)$_3$(bipy)] (13). To a solution of [Re(THF)(CO)$_3$(bipy)]BAr′$_4$ (**9**) (0.054 g, 0.040 mmol) in THF cooled to −78 °C was added a LiC≡CSiMe$_3$ solution prepared in situ by reaction of HC≡CSiMe$_3$ (5.6 μL, 0.040 mmol) and ^{n}BuLi (25 μL of a 1.6 M solution in hexane, 0.040 mmol) in THF at −78 °C. The mixture was stirred for 15 min, and the workup was as described for **12**. Compound **13** was obtained as an orange solid. Yield: 0.015 g, 71%. IR (THF): 2038 ($\nu_{C\equiv C}$); 2000, 1903 (ν_{CO}). ^{1}H NMR: 9.01, 8.21, 7.81, 7.52 [m, 2H each, bipy], −0.30 [s, 3H, $SiMe_3$]. Anal. Calcd for $C_{18}H_{17}N_2O_3ReSi$: C, 41.28; H, 3.27; N, 5.34. Found: C, 41.41; H, 3.32; N, 5.41.

Aziridination Reaction. To a solution of [Re(THF)(CO)$_3$(bipy)]BAr′$_4$ (**9**) (0.026 g, 0.019 mmol) in CH_2Cl_2 (20 mL) was added 2,6 di-*tert*-butylpyridine (10 μL, 0.038 mmol), benzylideneaniline (0.345 g, 1.903 mmol), and EDA (0.2 mL, 1.903 mmol). The mixture was stirred under nitrogen for 8 h, and the volatiles were removed under vacuum. The ^{1}H NMR spectrum showed full conversion to a mixture of the *cis*-(carboxyethyl)-1,3-diphenylaziridine **A** (72%, ^{1}H NMR integration) and the enamines **B** and **C** (Scheme 5). *cis*-(Carboxyethyl)-1,3-diphenylaziridine (**A**). ^{1}H NMR ($CDCl_3$): 1.03 [t, 3H, J = 7.05 Hz, CH_3]; 3.25 [d, 1H, J = 6.8 Hz, CHPh]; 3.63 [d, 1H, J = 6.8 Hz, CHCO]; 3.97−4.13 [m, 2H, CH_2]; 6.90−7.58 [m, 10H, C_6H_5].

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Supporting Information Available: CIF file giving positional and thermal parameters, bond distances, and bond angles for **6a**, **6b**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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