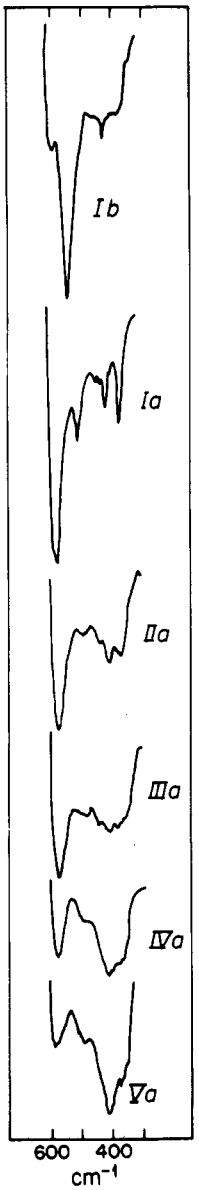

Figure 4. KBr disk IR spectra (300–600 cm^{-1}) for $(\mu_4\text{-O})(DENC)_4Cu_{4-x}(Ni(H_2O))_xH_6$ complexes.

centered at 3400 cm^{-1} in the IR spectra of the transmetalated products are due to coordinated water.[1-6]

Dieck[10] has shown that bands in the 300–600-cm^{-1} region are characteristic of the OM_4 unit in $(\mu_4\text{-O})N_4Cu_4X_6$ complexes, where N is a monodentate ligand. Figure 4 shows that four such bands are resolved in Ia, while broader bands at lower frequency are exhibited by Ib. The data for products IIa–Va in Figure 4 indicate a change of relative intensities of the bands at 580 cm^{-1} and 500, 460, 410, and 370 cm^{-1} with increasing x. The intense bands at 410 and 370 cm^{-1} are clearly due to ν_{Ni-OH_2} with high absorptivity relative to those for ν_{OM_4}. The absorptivities of the latter are sufficient to obscure the band at 460 cm^{-1} in Ia. These spectra confirm the same basic core structures in complexes Ia–Va. The band at 520 cm^{-1} in Ib (X = Br, x = 0; Figure 4) decreases in intensity relative to bands at 410 and 370 cm^{-1} with increasing x. This is further confirmation of the assignment of the latter to ν_{Ni-OH_2}.

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Registry No. Ia, 90741-95-0; Ib, 95785-44-7; IIa, 101998-13-4; IIb, 101998-14-5; IIIa, 101998-15-6; IIIb, 101998-16-7; IVa, 102046-56-0; IVb, 101998-17-8; Va, 90742-00-0; Vb, 101998-18-9; $Ni(NS)_2$, 34214-73-8.

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A Sequential Double Arbuzov-like Demethylation of *cis*-$PtX_2(P(OMe)_3)_2$ by Added Halide Ion

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The classical Arbuzov rearrangement involves an alkyl-transfer reaction between an alkylated nucleophile and a phosphorus(III) ester to give an organophosphorus(V) compound. An analogous reaction can occur with a phosphite ligand complexed to a transition-metal ion. Now the nucleophile induces dealkylation of the coordinated alkyl phosphite, resulting in its conversion to a complexed phosphonato ligand.[1]

The halide-induced dealkylation of complexed phosphite ligands has been well documented, but double dealkylations using this technique have few precedents.[2] An interesting application of this reaction is the generation of a complexed phosphito ligand having negative charge on oxygen which can be homologated to a diphosphite by reaction with a halophosphine. Such a sequence has been used to prepare $(CO)_5W((MeO)_2POPPh_2)$ and similar complexes.[3] Conceptually, an analogous double sequence could be carried out with a d^8 metal phosphite complex to generate a "ligand" that has the potential to form bimetallic complexes.[4] Such a method has general appeal because one can realistically place a wide variety of substituents on the phosphorus ligating atoms and also because one has the potential to synthesize heterobimetallic A-frame complexes with each metal at specific phosphorus ligating sites.

This paper describes our successful conversion of the compound *cis*-$PtCl_2(P(OMe)_3)_2$ into $PtCl_2(P(OMe)_3)(OP(OMe)_2)^-$ and then into $PtCl_2((OP(OMe)_2)_2)H^-$ using chloride ion as nucleophile. Each anionic complex can be separately identified and isolated, and we then use our spectral data to try to ascertain the charge localization in these complexes.

Experimental Section

The complexes *cis*-$PtCl_2(P(OMe)_3)_2$ and *cis*-$PtI_2(P(OMe)_3)_2$ were prepared by the literature method.[5] Melting points were measured on a Fisher-Johns apparatus and are uncorrected. Conductivity measurements were made on a Model RC 1682 conductivity bridge with platinum black electrodes. Microanalyses were carried out by Galbraith Inc., Knoxville, TN. Nuclear magnetic resonance spectra were measured on a Bruker AC 200 NMR spectrometer. Tetraphenylarsonium iodide was prepared by mixing aqueous solutions of Ph_4AsCl and NaI. The precipitated product was washed sequentially with water, acetone, and diethyl ether and was then air-dried. Acetonitrile was dried by continuous distillation from CaH_2. CD_3CN (Aldrich) was used as supplied.

Tetraphenylarsonium *cis*-Dichloro(dimethyl phosphonato)(trimethyl phosphite)platinum(II) (1). A 25-mL round-bottom flask, fitted with a reflux condenser, containing *cis*-$PtCl_2(P(OMe)_3)_2$ (104 mg, 0.202 mmol) and tetraphenylarsonium chloride (vacuum-dried at 110 °C) (254 mg, 0.606 mmol) was placed in an oil bath at 63 °C. Just sufficient CH_3CN (ca. 1 mL) was added to give a solution that was saturated when hot. After 25 min the solvent was removed on a rotary evaporator. To the solid was added CH_2Cl_2 (5 mL), and the solution was washed with water (3 × 5 mL). The CH_2Cl_2 solvent was removed under vacuum, and the residue was then vacuum-dried for 5 min and redissolved in acetone. Excess Ph_4AsCl was precipitated from the solution by addition of hexane until an oil just began to form (the solution remained cloudy), at which time the mixture was centrifuged. Solvent removal yielded an oil that on stirring in a mixture of hexane and ether (1:1) gave a colorless solid.

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Table I. NMR Spectral Data[a]

	$\delta(^1H)$	$^3J + {}^5J(PH)$, Hz	$\delta(^{13}C)$	$^2J + {}^4J(PC)$, Hz	$\delta(^{31}P)$	$^1J(PtP)$, Hz	$\delta(^{195}Pt)$
cis-$PtCl_2(P(OMe)_3)_2$	3.79	12.7	54.8	<1	74.3	5705	−4342.5
cis-$PtCl_2(OP_A(OMe)_2)(P_B(OMe)_3)^-$ (**1**)	3.66 (9 H) (B)	12.9 (B)	53.7 (B)	2.7	82.0 (B)	6608 (B)	−4293.5
	3.40 (6 H) (A)	12.1 (A)	50.3 (A)	6.0	30.4 (A)	5020 (A)	
					($^2J(P_AP_B)$ = 19 Hz)		
cis-$PtCl_2((OP(OMe)_2)_2H)^-$ (**2**)	3.55	12.9	52.3	<1	60.0	5422	−4348.2
cis-$PtI_2(P(OMe)_3)_2$	3.77	13.1	54.6	4.2	77.8	5495	−5056.1
cis-$PtI_2(OP_A(OMe)_2)(P_B(OMe)_3)^-$ (**3**)	3.67 (9 H) (B)	13.1 (B)	53.6 (B)	2.5	83.4 (B)	6425 (B)	−4892.5
	3.41 (6 H) (A)	12.3 (A)	50.3 (A)	6.3	36.8 (A)	4898 (A)	
					($^2J(P_AP_B)$ = 3 Hz)		
cis-$PtI_2((OP(OMe)_2)_2H)^-$ (**4**)	3.53	13.5	51.7	<1	64.7	5253	−4967.8
cis-$PtClI(OP_A(OMe)_2)(P_B(OMe)_3)^-$[b] (**5**)					78.0 (B)		
					34.4 (A)		
					($^2J(P_AP_B)$ = 9 Hz)		
cis-$PtICl(OP_A(OMe)_2)(P_B(OMe)_3)^-$[b] (**6**)					86.8 (B)		
					35.7 (A)		
					($^2J(P_AP_B)$ = 8 Hz)		
cis-$PtClI((OP(OMe)_2)_2H)^-$ (**7**)					65.8 (B)		
					58.8 (A)		
					($^2J(P_AP_B)$ = 23 Hz)		

[a] References used: ^1H (CD_2HCN = 1.93 ppm), ^{13}C (CD_3CN = 0.3 ppm), ^{31}P (H_3PO_4 = 0 ppm for each solvent), ^{195}Pt (H_2PtCl_6 = 0 ppm). Downfield positive shifts. [b] The stereochemistries of this pair of isomers cannot be definitively identified.

After 12 h the supernatant liquid was removed, and the product was vacuum-dried for 40 min to give a colorless powder: yield 152 mg (85%); mp 90–98 °C; Λ_M = 87.8 $cm^2\ \Omega^{-1}\ mol^{-1}$ (CH_3NO_2), typical of a 1:1 electrolyte.[6] Anal. Calcd for $C_{29}H_{35}AsCl_2O_6P_2Pt$: C, 39.2; H, 4.04; Cl, 7.98. Found: C, 39.4; H, 3.97; Cl, 8.02.

Tetraphenylarsonium *cis*-Dichloro(dimethyl phosphonato)(dimethyl phosphite)platinum(II) (2). A 25-mL round-bottom flask, fitted with a reflux condenser, containing *cis*-$PtCl_2(P(OMe)_3)_2$ (43 mg, 0.084 mmol) and tetraphenylarsonium chloride (175 mg, 0.42 mmol) was placed in an oil bath at 95 °C. Just sufficient dry CH_3CN was added to form a solution that was saturated when hot, although if necessary additional small aliquots of solvent may need to be added during the reaction. After 6 h the solvent was evaporated on a rotary evaporator, and the solid was extracted with acetone (2 × 3 mL) to remove Ph_4AsCl. The solvent was again evaporated, and the residue was dissolved in CH_2Cl_2. Addition of *i*-PrOH followed by evaporation of the CH_2Cl_2 gave the complex as a pale yellow solid: yield 28 mg (39%); mp 198–200 °C. Anal. Calcd for $C_{28}H_{33}AsCl_2O_6P_2Pt$: C, 38.7; H, 3.80; Cl, 8.18. Found: C, 38.6; H, 3.98; Cl, 7.93.

Tetraphenylarsonium *cis*-Diiodo(dimethyl phosphonato)(trimethyl phosphite)platinum(II) (3). This complex was prepared as a solution in acetonitrile either by treating $(Ph_4As)[PtCl_2(P(OMe)_3)(OP(OMe)_2)]$ with tetraphenylarsonium iodide, and following the spectral changes by $^{31}P\{^1H\}$ NMR spectroscopy, or by reacting *cis*-$PtI_2(P(OMe)_3)_2$ (427 mg, 0.61 mmol) with tetraphenylarsonium iodide (328 mg, 0.64 mmol) in CD_3CN solvent at 91 °C in a 10-mm NMR tube. The reaction was again followed by $^{31}P\{^1H\}$ NMR spectroscopy for 2 h, after which the conversion was complete. The complex can be precipitated by the addition of diethyl ether.

If *n*-Pr_4NI was used in place of Ph_4AsI, the reaction could be carried out at ambient temperature in 48 h. In the demethylation reactions, the compound CH_3I (^1H NMR δ 2.1; ^{13}C NMR δ −22.4) was formed in stoichiometric amounts.

Tetraphenylarsonium *cis*-Diiodo(dimethyl phosphonato)(dimethyl phosphite)platinum(II) (4). This complex was prepared as a solution in acetone solvent either by treating $(Ph_4As)[PtCl_2(OP(OMe)_2)_2)H]$ with sodium iodide, and following the spectral changes by $^{31}P\{^1H\}$ NMR spectroscopy, or by reacting *cis*-$PtI_2(P(OMe)_3)_2$ (427 mg, 0.61 mmol) with tetraphenylarsonium iodide (1.3 g, 2.4 mmol) in CD_3CN solvent in a 10-mm NMR tube at 91 °C. The reaction was followed by $^{31}P\{^1H\}$ NMR spectroscopy, which showed complete conversion to product after 9 h. Evaporation of the solvent followed by extraction with CH_2Cl_2 gave a solution free of Ph_4AsI. The complex is insoluble in diethyl ether.

Mixed-Halide Complexes (5–7). When $Ph_4As[cis\text{-}PtCl_2(OP(OMe)_2)(P(OMe)_3)]$ was treated with excess Ph_4AsI in acetonitrile solvent for 12 h at 42 °C, a solution containing the mixed-halide complexes **5–7** was formed. The species were detected by $^{31}P\{^1H\}$ NMR spectroscopy.

Results and Discussion

The complex $PtCl_2(P(OMe)_3)_2$ was readily prepared by the literature method,[5] and its purity was checked by $^{31}P\{^1H\}$ NMR spectroscopy. The complex $PtI_2(P(OMe)_3)_2$ was also prepared from the dichloro complex by metathetical replacement with sodium iodide. When these complexes are dissolved in the coordinating high dielectric constant solvent acetonitrile, addition of the appropriate halide ion (X^- = Cl^- or I^-) to the solution results in nucleophilic attack at the methyl carbon. Stepwise demethylation occurs to give $PtX_2(OP(OMe)_2)(P(OMe)_3)^-$ and then $PtX_2((OP(OMe)_2)_2H)^-$ (X = Cl, I) (eq 1).[7] We observe

$$cis\text{-}PtX_2(P(OMe)_3)_2 \xrightarrow[-MeX]{X^-} cis\text{-}PtX_2(OP(OMe)_2)(P(OMe)_3)^- \xrightarrow[-MeX]{X^-,\ H^+} cis\text{-}PtX_2(OP(OMe)_2)_2H^- \quad (1)$$

1, X = Cl; **3**, X = I; **2**, X = Cl; **4**, X = I

quantitative monodemethylation to $PtX_2(OP(OMe)_2)(P(OMe)_3)^-$ after 25 min at 63 °C (X = Cl; **1**) or after 2 h at 91 °C (X = I; **3**). If double demethylation is desired, the reactions require heating for 6 h at 95 °C (X = Cl; **2**) or for 9 h at 91 °C (X = I; **4**). These changes can be followed in solution by ^1H, ^{13}C, or ^{31}P NMR spectroscopy, and these spectral data are collected in Table I. The assignment of the peaks in the ^{31}P NMR spectrum due to the $OP(OMe)_2$ group was made by the presence of septet multiplicity ($^3J(PH)$ = 12 Hz) in the hydrogen-coupled spectrum; by comparison, the peak due to $P(OMe)_3$ has a dectet multiplicity. Stoichiometric quantities of MeCl (δ 3.0) or MeI (δ 2.1) are also formed in the reaction, and can be observed in the ^1H NMR spectrum.

The loss of a second methyl group occurs in a successive reaction. This second methyl group is also lost as a consequence of nucleophilic attack at the complexed $P(OMe)_3$. This conversion causes the phosphorus nuclei in the final product complex to again become equivalent. Isolation of these products from the reaction using Ph_4AsX (X = Cl, I) as nucleophile shows them to be the monoprotonated complexes $Ph_4As[cis\text{-}PtX_2((OP(OMe)_2)_2H)]$, rather than the anticipated dianion. This stoichiometry is confirmed by integration of the phenyl and methyl resonances in the ^1H NMR spectrum and by combustion analysis of the dichloro compound **2**. Apparently the initially formed dianion *cis*-$PtX_2(OP(OMe)_2)_2^{2-}$ undergoes protonation from traces of water present

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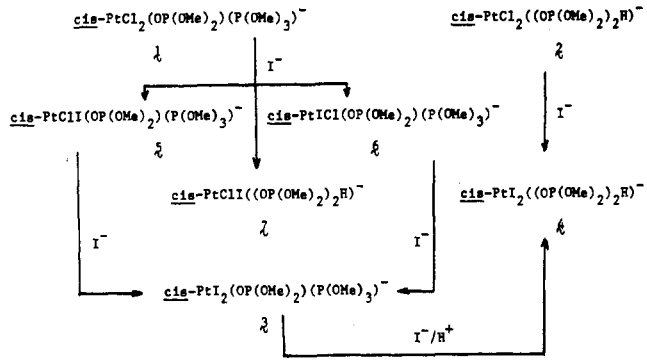
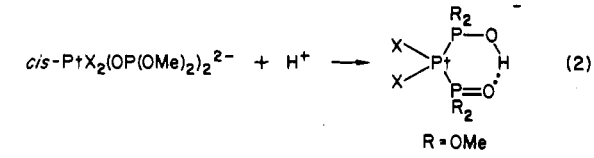
Scheme I



in the reaction mixture to give the observed monoanionic product complexes **2** and **4** (eq 2).[8] We do not observe a resonance due

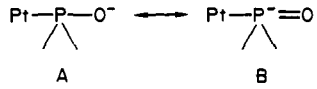


(2)

to the single acidic proton at the expected large downfield shift position, but such resonances are frequently unobserved in these complexes due to exchange.[7]

If halide nucleophiles other than those complexed to platinum are used, mixed-halo complexes are obtained (Scheme I). These complexes have been characterized by $^{31}P\{^1H\}$ NMR spectroscopy. We cannot, however, assign the stereochemistries of complexes **5** and **6** with any degree of certainty.

In practice, therefore, the route to prepare bifunctional ligands through the dianionic complex is not a viable one for the assemblage of heterobimetallic complexes. For the P-bonded phosphinito ligand of molybdenum(0) it is apparent that the negative charge resides primarily on oxygen, but for these divalent-platinum complexes this localization is less likely. We can now use the spectral data for **1** and **3** to assess whether the dimethyl phosphito ligand complexed to platinum(II) is best represented by tautomer A or B. The $^{31}P\{^1H\}$ shift data with the resonance for the com-



plexed dimethyl phosphito ligand at δ 30.4 (**1**) and δ 36.8 (**3**) show unambiguously that the phosphonato tautomer B is the canonical form that corresponds with this large upfield shift.[1] Thus in these platinum(II) complexes the negative charge is not localized on oxygen. The changes in $\delta(^{195}Pt)$ are small, as are changes in $\delta(^1H)$ and $\delta(^{13}C)$. This suggests that no significant changes occur in the shielding density at the Pt nucleus.[9] In support of this premise, we find that treating complex **3** with Ph_2PCl gives impure products that show, by $^{31}P\{^1H\}$ NMR spectroscopy, substitution at platinum by the phosphine. It is apparent therefore that Wong's procedure cannot be used with platinum(II) complexes to effect template syntheses of bridging *P,P*-ligands.

Registry No. **1**, 101997-95-9; **2**, 101997-97-1; **3**, 101997-99-3; **4**, 101998-01-0; **5**, 101998-02-1; **6**, 102129-57-7; **7**, 101998-03-2; *cis*-$PtCl_2(P(OMe)_3)_2$, 28374-51-8; *cis*-$PtI_2(P(OMe)_3)_2$, 28374-52-9; $P(OMe)_3$, 121-45-9; Ph_4AsCl, 507-28-8; Ph_4AsI, 7422-32-4.

(8) The hydroxylated complex is formed even when dried acetonitrile solvent is used in the reaction. Under these experimental conditions the hydrogen source is water in Ph_4AsX, since we find by ^1H NMR spectroscopy that vacuum-dried samples of purified salt contain small quantities of water.

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Synthesis and Properties of (Ethylenebis(dithiocarbamato))diorganotin(IV) Complexes. Structure of $[(t\text{-Bu})_2Sn(ebdtc)]_2\cdot 4THF$

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Interest in dithiocarbamate complexes of diorganotin(IV) species[1-5] arises in part because of their varied structures[6-14] and because of their biological activity.[15,16] Crystallographic studies of these complexes[6-9] have revealed a variety of coordination geometries about the Sn atom, ranging from tetrahedral to distorted octahedral, as well as dithiocarbamate ligands that are either anisobidentate[8,9] or monodentate.[6,7] In an effort to extend this chemistry we have prepared the first organotin(IV) complexes of the ethylenebis(dithiocarbamate) ligand $^-S_2CNHCH_2CH_2NHCS_2^-$, (ebdtc), a ligand that is potentially tetradentate. The sodium salt of ebdtc displays biological activity a few times greater than that of the sodium salt of dimethyldithiocarbamic acid.[16] Here we report the syntheses and properties of diphenyl- and di-*tert*-butyltin(IV) complexes of ebdtc together with a crystal structure of the di-*tert*-butyltin(IV) complex.

Experimental Section

All preparations were performed under a dinitrogen atmosphere with the use of standard Schlenkware techniques. Reagent grade chemicals were used without further purification. Chemical analyses were carried out by the Chemical Analysis Laboratory at KAIST. Mass spectra were recorded on a Varian Model 212 GC-MASS system (THF solution). ^1H-NMR spectra were recorded on fresh samples in Me_2SO-d_6 on a JEOL JNM-PMX 60 or a Varian FT-80A spectrometer with Me_4Si as the reference. The infrared spectra in the 300–4000-cm^{-1} region were measured on KBr pellets with a Perkin-Elmer 283B spectrophotometer.

Preparation of the ebdtc Ligand. A solution of $Na_2(ebdtc)$ was prepared in the following manner:[17] to 3.0 g of 1,2-diaminoethane dissolved in 30 g of H_2O was added 8.0 g of CS_2 slowly with stirring. The solution was maintained at 35 °C and was slowly neutralized by addition of concentrated NaOH solution. To this reaction mixture was added ethanol until crystals started to form, and the mixture was left overnight. The white crystalline solid thus obtained was recrystallized from a H_2O–EtOH solvent pair (1:2), to produce the hexahydrate in 79% yield. Mp: 82 °C. Anal. Calcd for $C_4H_6N_2Na_2S_4\cdot 6H_2O$: C, 13.16; H, 4.94; N, 7.69; CS_2, 41.7. Found: C, 13.50; H, 4.90; N, 7.72; CS_2, 41.7.

Preparation of $(t\text{-Bu})_2Sn(ebdtc)$. $Na_2(ebdtc)$ (3 mmol) in 100 mL of ethanol was added dropwise to an equimolar solution of di-*tert*-butyltin dichloride in 100 mL of ethanol. After the reaction mixture was cooled to about 0 °C, the NaCl formed was removed by filtration. The filtrate was condensed to approximately 100 mL with a rotary evaporator, and then *n*-hexane was added slowly to the filtrate to precipitate the product. The resultant off-white solid was recrystallized from a benzene–petroleum ether (1:1) solvent pair. The monobenzene-solvate crystalline solid (mp 189 °C) was obtained in 72% yield. ^1H NMR (δ): 1.5 (s, *t*-Bu), 3.5 (s, CH_2), 7.3 (s, Ph), 10.1 (br, NH). IR (cm^{-1}): ν(C–N), 1525 (s), 1505 (s); ν(C–S), 975 (s), 950 (sh); ν(Sn–S), 390 (s). Anal. Calcd for $C_{12}H_{24}N_2S_4Sn\cdot C_6H_6$: C, 41.43; H, 5.75; N, 5.37; Sn, 22.8. Found: C, 41.20; H, 5.83; N, 5.13; Sn, 22.5.

When recrystallization is performed in a THF–*n*-hexane solvent pair, the THF-solvated product $(t\text{-Bu})_2Sn(ebdtc)\cdot 2THF$ is obtained. ^1H NMR (δ): 1.5 (s, *t*-Bu), 1.8 (qui, THF), 3.5 (s, CH_2), 3.7 (t, THF), 10.1 (br, NH). IR (cm^{-1}): ν(C–N), 1520 (s), 1495 (s); ν(C–S), 975 (s), 950 (sh); ν(Sn–S) 390 (s). The composition of $[(t\text{-Bu})_2Sn(ebdtc)]_2\cdot 4THF$ was established in the X-ray study.

Preparation of $Ph_2Sn(ebdtc)$. To a solution of diphenyltin(IV) dichloride (3 mmol) in 100 mL of ethanol was added an equimolar ethanol solution of $Na_2(ebdtc)$. After removal of NaCl and concentration of the filtrate, *n*-hexane was added. The resultant solid was recrystalized from a THF–petroleum ether pair (1:3) to yield the pale yellow product (mp 113 °C) in 78% yield. ^1H NMR (δ): 3.5 (s, CH_2), 7.3 (m, Ph), 7.8 (br,

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