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Mercuration of Schiff Bases of Substituted Benzylideneanilines

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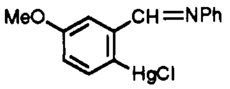
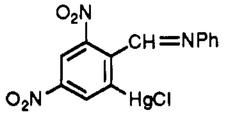
As part of an effort to investigate substituent effects on the intramolecular coordination between N and Hg, the mercuration of 36 substituted benzylideneanilines was studied. The structure characterization of the products by IR, ^{1}H NMR, ^{13}C NMR, and MS indicates that for all of the reactions examined, the mercury is directed to the ortho position of the *N*-phenyl ring or the para position of the *N*-phenyl ring when these sites are not occupied by a substituent. The position of the HgCl group in the mercurated product of *N*-(4-nitrobenzylidene)-β-naphthylamine has been confirmed by single-crystal X-ray determination, which also provided circumstantial evidence for the existence of the N→ Hg intramolecular coordination with a four-membered ring. The possible mechanism of the reaction was proposed, in which the mercuration at the ortho position of the *N*-phenyl ring was facilitated by the imino moiety upon formation of a coordination complex with $Hg(OAc)_2$ in the first step, followed by a subsequent electrophilic substitution at the ortho position of the N-phenyl ring. This reaction is different from the metalation of benzylideneanilines by transition metals, in which the metal atom is usually directed to the ortho position of the *C*-phenyl ring, and provides a new example of the so-called "cyclometalation" reaction.

Over the last two decades, there has been a great deal of interest in the ortho-metalation reaction of substituted aromatic compounds in which nitrogen-containing groups act as electron donor ligands.[1] Numerous relevant organometallic intramolecular coordination compounds have been synthesized and some have been found to be useful in organic syntheses.[2] Until now, attention has been focused on the reactions of transition metals (e.g. Pd, Pt etc.). Compared to the transition metals, the coordinating ability of the nontransition metals (e.g. Hg, Sn, etc.) is weak. The direct orthomercuration reactions are primarily restricted to the reaction of substituted azobenzenes[3] and phenylhydrazones,[4] in which nitrogen donor ligands facilitate the formation of the C–Hg σ-bond. Work on mercuration of Schiff bases of the substituted benzylideneanilines was first published by Singh et al.,[5] where two mercurated derivatives were reported.





In their molecules, mercury is considered to be bonded to the ortho position of the *C*-phenyl ring. Because of the weak coordinating ability of mercury and specific electron population distribution of benzylideneaniline,[6] the mercury is very likely directed to the ortho position of the *N*-phenyl ring and, as a result, may form an intramolecular coordination via a four-membered ring. In our opinion, the structure of the mercurated Schiff bases reported by Singh et al. may be incorrect. It is known that in arylmercury compounds ortho substituents with p- or π-electrons have substantial effects on reaction rates and spectral properties.[7] As part of an effort to investigate substitutent effects on the intramolecular coordination between N and Hg, mercuration of some substituted benzylideneanilines has been studied. The present paper reports the results of the direct mercuration of substituted benzylideneanilines, effects of substituents, solvents, and electrophiles on this reaction, and the possible mechanism of the reaction.

Results and Discussion

We began our investigation with the Schiff bases (**1a–7a**) since the product structure can be easily identified by ^{1}H NMR spectroscopy due to the presence of the strong electron-withdrawing NO_2 group in the *C*-phenyl ring. The mercuric chlorides of the corresponding Schiff bases (**1b–7b**) were synthesized by in situ reaction of Schiff bases with mercuric acetate (1:1 molar ratio) in refluxing dry methanol for 4 h, followed by the addition of lithium chloride. Reactions were carried out on a 5-mmol scale, and the initial concentration of each substrate was kept the same (~0.1 M). For all the new compounds prepared, compositions and structures were determined and confirmed by elemental analysis, IR, NMR, and MS.

Characterization of Products. ^{1}H NMR. The elemental analyses and IR spectra indicated that all the mercurated derivatives are composed of one Schiff base unit and one HgCl group except for **3b** and **10b** where two

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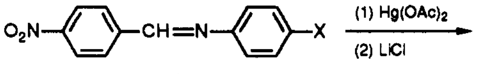
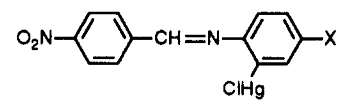


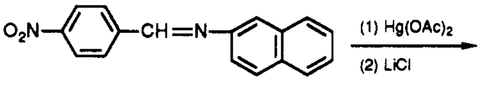
1a–6a

1a, X = CH_3; **2a**, X = CH_3O; **3a**, X = H;
4a, X = Cl; **5a**, X = Br; **6a**, X = I

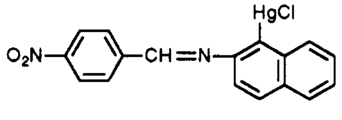


1b–6b

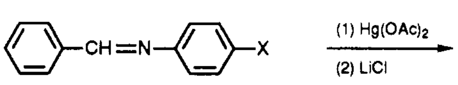
1b, X = CH_3; **2b**, X = CH_3O; **3b**, X = HgCl;
4b, X = Cl; **5b**, X = Br; **6b**, X = I



7a

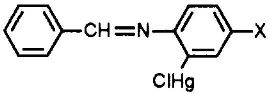


7b



8a–13a

8a, X = CH_3; **9a**, X = CH_3O; **10a**, X = H;
11a, X = Cl; **12a**, X = Br; **13a**, X = I



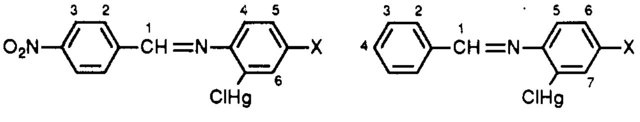
8b–13b

8b, X = CH_3; **9a**, X = CH_3O; **10b**, X = HgCl;
11b, X = Cl; **12b**, X = Br; **13b**, X = I

HgCl groups are present. The position of the mercury atom was determined by ^1H NMR. As expected, the aromatic region of the spectrum for each compound contains a group of left–right symmetrical multiplet peaks (4 H) characterizing the four-spin AA′BB′ system at lower field due to the electron-withdrawing effect of the nitro group. Furthermore, it was found that the substituents X have no effect on the chemical shift values of these protons. So, these signals can only be assigned to the *C*-phenyl protons (H2, H3). The remaining two doublets (2 H) and a doublet of doublets (1 H) which belong to the three-spin ABX system at higher field correspond to the three *N*-phenyl protons, for which the δ values vary considerably with different substituents X. The assignment of ^1H NMR spectra (Table I) for the Schiff base type organomercury compounds **1b–7b** showed that the mercury is directed to the ortho position of the *N*-phenyl ring rather than the ortho position of the *C*-phenyl ring. Further investigation of the ^1H NMR spectra of mercurated products **8b–13b** gave the same conclusion. In the cases of **3a** and **10a**, the mercury atom is also directed to the para position of the *N*-phenyl ring, in addition to the ortho position. This can be observed from the spectral data of **3b** and **10b**.

The NOE spectrum of compound **1b** was obtained by irradiation of the methyl proton at 2.42 ppm and the methine proton at 9.00 ppm, respectively. The significant enhancements of the signals at 7.28 (10%) and 7.53 ppm (10%) identify these as protons H5 and H6, respectively, closest to the methyl being irradiated, and correspondingly, the enhancement of the signals at 8.25 ppm (12.5%) identified these peaks as due to proton H2, closest to the methine proton being irradiated. So, the results of the NOE experiment support the assignment by ^1H NMR.

Table I. ^1H NMR Data for Compounds 1b–13b[a]



1b–7b **8b–13b**

compd	H-1	H-2	H-3	H-4	H-5	H-6	H-7
1b	9.00	8.25	8.46	7.50	7.28	7.53	
2b	8.99	8.22	8.45	7.64	7.03	7.35	
3b	8.95	8.22	8.45	7.50	7.50	7.68	
4b[b]							
5b	8.98	8.25	8.47	7.53	7.60	7.89	
6b	8.99	8.26	8.49	7.30	7.75	8.05	
7b	9.30	8.34	8.50				
8b	8.84	8.00	7.60	7.61	7.44	7.24	7.49
9b	8.84	8.03	7.63	7.64	7.57	7.02	7.42
10b	8.83	8.00	7.63	7.64	7.41	7.49	7.60
1b	8.84	8.04	7.64	7.64	7.49	7.48	7.74
12b	8.84	8.04	7.62	7.63	7.45	7.61	7.87
13b	8.82	8.03	7.64	7.64	7.31	7.76	8.05

[a] All data recorded in DMSO-d_6 at 20 °C. [b] This compound cannot be dissolved in DMSO-d_6.

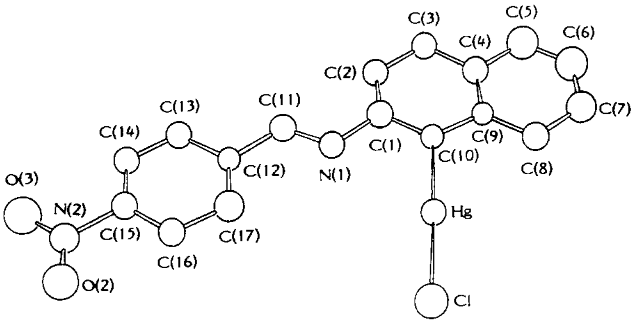


Figure 1. Drawing of structure of **7b**.

^{13}C NMR. It was observed from the $^{13}C\{^1H\}$ NMR spectra of the aromatic carbons of organomercurials **8b–13b**, that the chemical shift values of five tertiary and one quarternary carbons were virtually not affected by different substituents, whereas the δ values of the other three tertiary and three quarternary carbons varied markedly with different substituents. Table II lists the assigned ^{13}C NMR spectra for **8b–13b**. An examination of the variations of the chemical shifts of C6, C7, and C11 with different substituents shows that electron-withdrawing groups cause a downfield shift and that electron-donating groups cause an upfield shift, respectively. The chemical shifts of C6 and C7 exhibit a good linear correlation with the Brown σ_p^+ and σ_m^+ constants, respectively. Thus by regression analyses, we have the following equations:

$$\delta(^{13}C6) = 153.1 + 7.78\sigma_p^+ \qquad r = 0.989 \qquad (1)$$

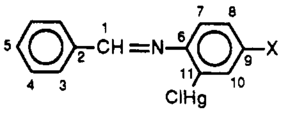
$$\delta(^{13}C7) = 117.2 + 5.40\sigma_m^+ \qquad r = 0.940 \qquad (2)$$

There is no linear correlation between $\delta(^{13}C11)$ and σ_m^+, probably due to the N→Hg intramolecular coordination which affects the electron distribution on the C11 atom. The δ values of the methine carbon (C1) fit the Hammett constants reasonably well. The following relationship was obtained by linear regression analysis:

$$\delta(^{13}C1) = 159.0 + 6.27\sigma_p \qquad r = 0.971 \qquad (3)$$

MS. For the mercuration of **1a–13a**, if the mercury atom was directed either to the ortho positions of the *C*-phenyl ring (C3) or of the *N*-phenyl ring (C7), the cor-

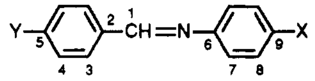
Table II. $^{13}C\{^1H\}$ **NMR Data for Compounds 8b–13b**[a]

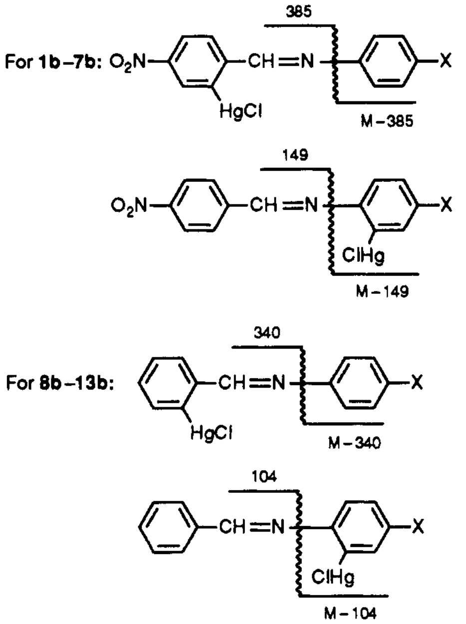


compd	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11
8b	158.5	135.5	128.8	128.4	131.3	151.5	116.8	129.7	136.7	137.1	151.4
9b	156.9	136.3	128.8	128.2	131.1	146.7	117.4	121.6	157.8	114.3	154.0
10b	159.6	136.0	128.8	128.5	131.5	153.5	117.1	137.0	151.0	144.1	149.8
11b	160.3	135.9	128.9	128.7	131.7	153.7	118.8	128.7	130.6	135.9	152.9
12b	160.4	135.9	128.9	128.6	131.7	154.1	119.3	131.5	129.5	138.7	153.6
13b	160.3	135.9	128.9	128.7	131.7	154.3	119.8	137.3	92.5	144.7	153.7

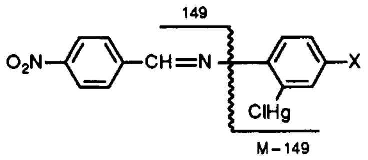
[a] All data recorded in DMSO-d_6 at 20 °C.

responding different fragment ions should be observed in the mass spectra.

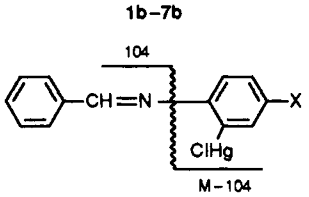




It was found that the ions *m/e* M – 149 and *M* – 104 are present, but the ions *m/e* 385 and 340 are absent in the spectra of **1b–7b** and **8b–13b**, respectively. Therefore, mercury attack on the ortho position of the *C*-phenyl ring can be eliminated. In the case of **6b**, the cation *m/e* M – 149 is not formed, probably due to the high melting point and the weak C–I bond strength of **6b**. The fragmentation behavior observed for **1b–13b** can be expressed as follows:



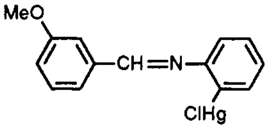
1b–7b



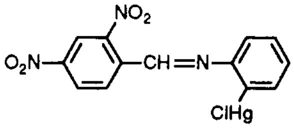
8b–13b

As expected, the mercury is directed into the ortho position of the *N*-phenyl ring.

In order to reexamine the results reported by Singh et al., the mass spectra of mercurated derivatives (**14b**, **15b**) of (3-methoxybenzylidene)aniline and (2,4-dinitrobenzylidene)aniline were recorded. The appearance of an *m/e* 313 peak indicated that the mercury atom was directed into the *N*-phenyl ring. Further examination of the $^{13}C\{^1H\}$ NMR spectrum of **14b** showed 13 peaks in the aromatic region. This also led us to believe that the mercury was directed to the ortho position of the *N*-phenyl ring.



14b



15b

X-ray Crystallographic Results for 7b. In order to confirm the position of HgCl on the naphthalene ring for compound **7b** and to provide at least circumstantial evidence for the existence of N→Hg intramolecular coordination in the mercurated Schiff bases, a single-crystal X-ray structure determination of **7b** was carried out. Crystals of **7b** suitable for X-ray analysis were obtained by slow recrystallization from 1,4-dioxane. Elemental analysis indicated that the crystals contain 0.5 molecule of crystalline 1,4-dioxane, which was also supported by thermoanalysis. The loss of weight for TG at 141 °C on the DTA curve is about 7.9%, which is equivalent to 0.5 mol of 1,4-dioxane. Another endothermal peak at 273 °C represents the melting of **7b**.

The crystal structure of **7b** is shown in Figure 1. The structure is thus confirmed as α-(chloromercurio)-*N*-(4-nitrobenzylidene)-β-naphthylamine. In other words, the HgCl is situated at the α-position of the β-naphthylamine unit. The oxygen atoms in 1,4-dioxane do not coordinate with the mercury atom and exist in the unit cell relying on van der Waals forces. The lengths of Hg–C10 [2.099 (9) Å] and Hg–Cl [2.303 (2) Å] are similar to those found in other organomercuric chlorides.[8] The bond angles of N1–C1–C10 [114.3 (8)°] and C1–C10–Hg [117.2 (2)°] are less than 120°, which may arise from a N→Hg interaction.

Structural Effect on the Reaction. Further investigation of the structural effects of the substrates (**16a–26a**) on mercuration revealed that, whether the *C*-phenyl ring bears an electron-donating group or an electron-withdrawing group, the mercury in the product molecules (**16b–26b**) is attached to the ortho position of the *N*-phenyl ring, without exception.

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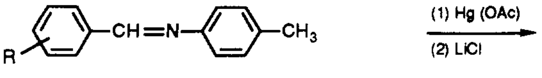
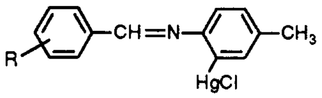


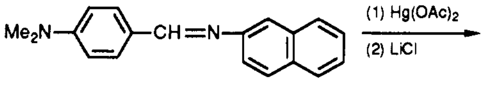
16a–26a

16a, R = *p*-NMe$_2$; **17a**, R = *p*-MeO; **18a**, R - 3,4-(MeO)$_2$; **19a**, R = *o*-MeO; **20a**, R = *p*-Cl; **21a**, R = *m*-Cl; **22a**, R = *o*-Cl; **23a**, R = *p*-Br; **24a**, R = *m*-Br; **25a**, R = *m*-NO$_2$; **26a**, R = *o*-NO$_2$

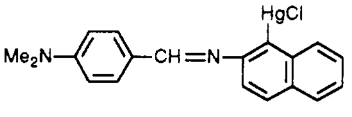


16b–26b

For the purpose of comparison with **7a**, mercuration of **27a** bearing a strong electron-donating NMe$_2$ group on the *C*-phenyl ring was carried out. It was found that the reaction took place at the same position as in **7a**.

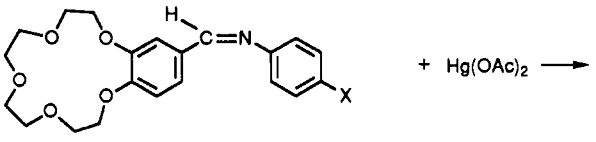


27a



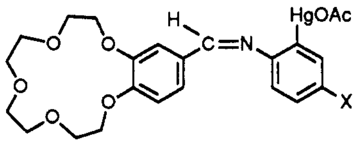
27b

We have tried to prepare 4′-(ClHg)-benzo-15-crown-5 from 4′-(H$_2$N)-benzo-15-crown-5 according to the literature method.[9] Instead, we isolated an unexpected novel complex with the composition [Na(B15C5)]$^+_2$[Hg$_2$Cl$_8$]$^{2-}$·H$_2$O.[10] Nonetheless, mercuration of the derivatives of benzo-15-crown-5 (**28a–31a**) revealed that the mercury was also directed into the ortho position of the *N*-phenyl ring as usual, without the formation of a coordination complex of Hg(OAc)$_2$ with the benzo-15-crown-5 unit.



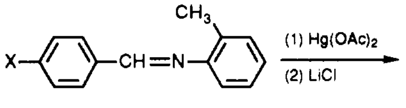
28a–31a

28a, X = CH$_3$; **29a**, X = CH$_3$O; **30a**, X = Cl; **31a**, X = Br

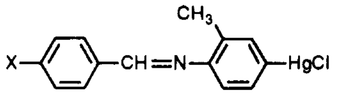


28b–31b

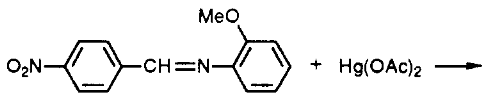
As mentioned previously, in the mercuration of **3a** and **10a**, dimercurials (**3b** and **10b**) were obtained as the main products. In order to understand the ortho substituent effect on this reaction, five ortho-substituted Schiff bases (**32a–36a**) were used in the mercuration reaction. When the ortho position of the *C*-phenyl ring was not occupied by a substituent and while the ortho position of the *N*-phenyl ring was substituted by a methyl group, the Schiff bases (**32a, 33a**) were mercurated in the para position of the *N*-phenyl ring; and if the ortho position of the *N*-phenyl ring was substituted by a methoxy group, the substrate (**34a**) was mercurated in both the ortho position and the para position of the *N*-phenyl ring. When the ortho position of *C*-phenyl ring was occupied by the nitro group (**35a, 36a**), the reaction took place in both the ortho position and the para position of the *N*-phenyl ring, no matter whether the ortho position of the *N*-phenyl was occupied by the methyl group or not.



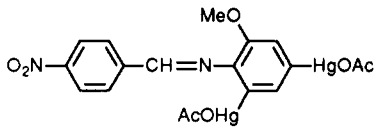
32a, X = H; **33a**, X = NO$_2$



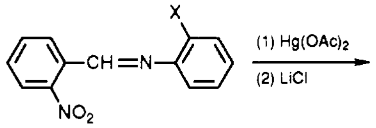
32b, 33b



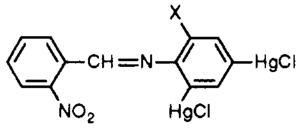
34a



34b

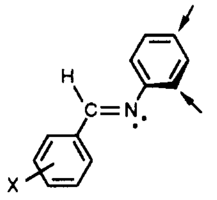


35a, X = H; **36a**, X = CH$_3$



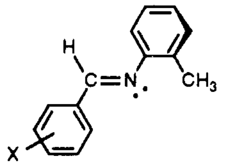
35b, 36b

The regioselectivity of the reaction can be interpreted in terms of the electron distribution and conformation of the substrates. In the cases of **3a, 10a**, and **35a**, mercuric acetate can attack both the ortho and para positions of the *N*-phenyl ring, because of the higher electron densities at those sites.[6]

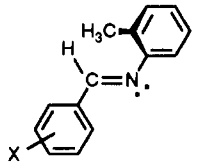


X = *p*-NO$_2$ (**3a**), H (**10a**), *o*-NO$_2$ (**35a**)

In the cases of **32a** and **33a**, however, the stable conformation is probably I rather than II, because electron repulsion from the shorter distance between the methine proton and the *o*-methyl protons disfavors II. Thus the *o*-methyl group may block coordination of the imino nitrogen atom with mercuric acetate and eliminate the the preference for attack at the ortho position of the *N*-phenyl



I



II

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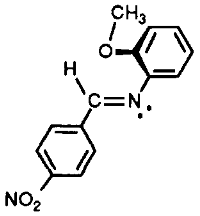
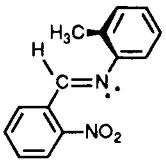
[9] Hu, H. W.; Ni, J. S.; Kao, T. Y. *Acta Chim. Sin. (Chin. Ed.)* **1979**, *37*, 9–13; *Chem. Abstr.* **1979**, *91*, 20645w.

[10] Tao, J. C.; Ding, K. L.; Wu, Y. J.; Zhu, Y. *Chin. J. Chem.* **1992**, *10*, 507–512.

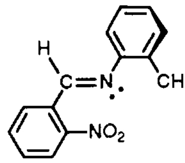
ring. If the *o*-methyl group in **33a** is replaced by a methoxy group, the preferred conformation of molecule **34a** is probably the same as in III, due to the longer distance between methine proton and methoxy oxygen. When the ortho position of the *C*-phenyl ring is substituted by a nitro group as in **36a**, the molecule will prefer to adopt conformation IV that relieves the possible repulsion between the nitro and methyl groups in the case of V. Therefore, the conformations of **34a** and **36a** have no signaficant effect on the coordination between N and Hg, and as a result, the mercury can be directed to the para position as well as to the ortho position of the *N*-phenyl ring.



III

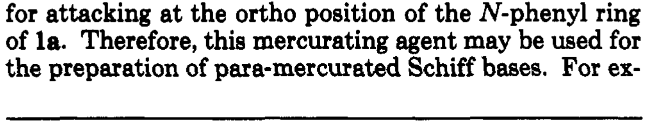


IV



V

Effects of Changing the Electrophile. When **1a** was treated with $HgCl_2$ in methanol and refluxed for 24 h, no reaction was observed. Perchloric acid, which can be used as a catalyst to accelerate the rate of aromatic mercuration,[11] has been successfully applied to the mercuration of azobenzene and its derivatives.[3b] Thus, an attempt was made to increase the rate of mercuration of Schiff base by adding a small amount of perchloric acid to the reaction system. Unfortunately, the color of the reaction mixture was changed from yellow to dark brown immediately upon the addition of perchloric acid, which was probably caused by oxidation of the Schiff bases by perchloric acid. In a further investigation of the effect of the electrophilic species on the reaction, $Hg(OAc)_2$·BTMAC (benzyltrimethylammonium chloride) was used as an electrophile instead of $Hg(OAc)_2$. The reaction proceeded rather slowly. When **1a** was treated with $Hg(OAc)_2$·BTMAC in methanol and refluxed for 24 h, the yield of reaction (without the addition of LiCl) was 75.8%, lower than that when $Hg(OAc)_2$ was used as the mercurating agent (refluxed in methanol for 4 h, yield 84.2%). In this reaction, the real electrophile is probably ClHgOAc, and the lower yield of the reaction may arise from its reduced coordinating ability to nitrogen and weakened electrophilicity for attacking at the ortho position of the *N*-phenyl ring of **1a**. Therefore, this mercurating agent may be used for the preparation of para-mercurated Schiff bases. For example, it reacts with $4'-O_2NC_6H_4CH{=}NC_6H_5$ (**3a**) to give, as expected, the para-mercurated derivative **37b** as the major product.

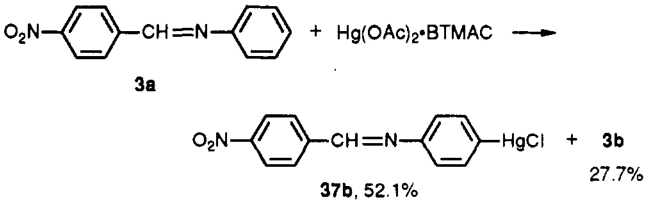


1a

1b, 75.8%

Table III. Solvent Effect on the Mercuration of 1a

	solvents					
	CH_3OH	C_2H_5OH	$C_4H_8O_2$	$CH_3OC_2H_4OH$	CH_2Cl_2	CH_3COOH
time (h)	4	4	4	4	4	24
temp (°C)	65	78	101	125	40	118
yield (%)	84.2	88.4	84.2	96.8	trace	0



3a

37b, 52.1%

27.7%

Solvent Effects on the Reaction. An examination of solvent effects on the mercuration reaction of **1a** (Table III) revealed that those which solvate HOAc better favor the reaction whereas those with weaker solvation ability inhibit the reaction. In HOAc alone, no reaction occurs. This suggests that the last step of the reaction, the conversion from σ-complex to the product, may be the rate-determining step, consistent with the general mechanism of aromatic electrophilic mercuration.[11]

Mechanism of the Reaction. Roling and co-workers reported a mercuration mechanism for azobenzene, in which the mercury is directed to the ortho position by coordinating with the azo nitrogen, followed by a subsequent electrophilic substitution.[3b] The mercuration of substituted phenylhydrazones was facilitated by a favorable attack of the n-electrons of the hydrazone imino moiety.[4d] The results obtained in this study of the mercuration reaction of Schiff bases of substituted benzylidenanilines lead us to conclude that in this reaction the mercury is directed to the ortho position of the *N*-phenyl ring by coordinating with the nitrogen atom followed by a subsequent electrophilic substitution (Scheme I). The mechanism embodies four seperate steps: (I) the coordination complex formation between $Hg(OAc)_2$ and the imino moiety, (II) the formation of a π-complex with the *N*-phenyl ring, (III) the conversion of the π-complex to a σ-complex, and (IV) the loss of HOAc from the σ-complex and the formation of the product. The coordination of imino nitrogen with mercury is present in the whole process of the ortho-mercuration.

Support of mercury coordination (step I) is found in the 1:1 complex formed between mercuric chloride and either 2-(phenylimino)ethyl butyrate[12] or *trans*-$PtCl(PEt_3)_2(CH{=}NC_6H_4\text{-}p\text{-}CH_3)$.[13] It is interesting to note that the mercuration of the second ortho position was not observed, either when 2 mol equiv of mercuric acetate was used with **1a** or when **1b** was treated separately with an additional 1 mol equiv of $Hg(OAc)_2$. This would be expected for involvement of the n-electrons in the formation of the ortho-mercurated derivative since they occupy the frontier orbital of the imino moiety and thus are likely to coordinate with the mercury atom in $Hg(OAc)_2$. This can also be illustrated on the basis of regioselectivity of mercuration for **32a**–**36a**. The evidence of the π-complex formation in the mercuration reaction has not been reported, but the intramolecular mercury–arene coordination is conceivable.

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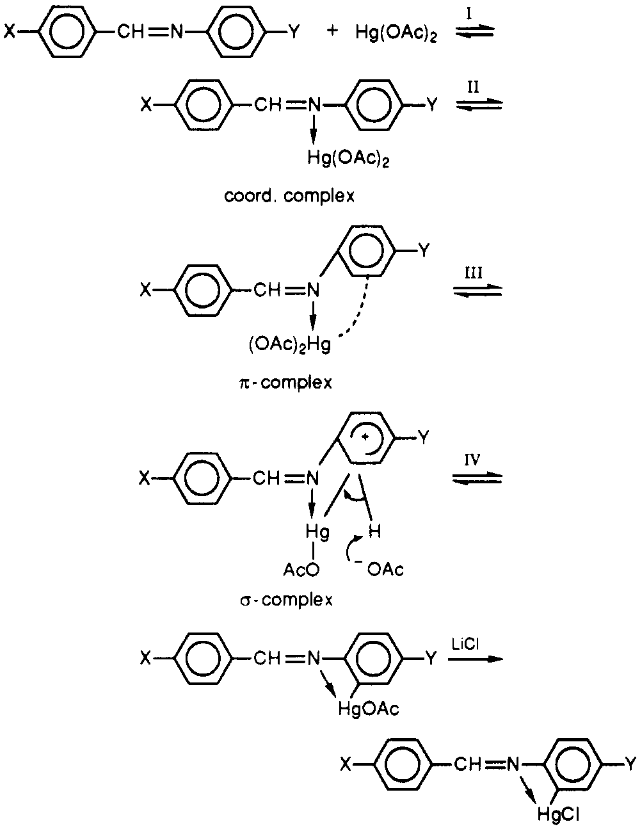
(11) Bamford, C. H.; Tipper, C. F. H. *Comprehensive Chemical Kinetics*; Elservier Publishing Co.: New York, 1972; Vol. 13, pp 186–194.

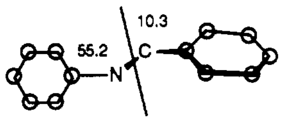
(12) Thakob, V. M.; Shau, R. C. *J. Indian Chem. Soc.* **1949**, *26*, 251–253.

(13) Bonati, F.; Clark, H. C. *Can. J. Chem.* **1979**, *57*, 483–486.

Scheme I. Probable Mechanism for Mercuration of Schiff Bases



For example, ^{199}Hg NMR studies on γ-(arylpropyl)mercury compounds have disclosed the presence of mercury–arene coordination.[14] It is well-known that the ground-state molecule of azobenzene is planar. In contrast, the molecular conformation of benzylideneaniline is different from that of azobenzene: the twist angles of the *N*-phenyl ring and the *C*-phenyl out of the C—N=C—C plane are 55.2 and 10.3°, respectively.[15]



Therefore, benzylideneaniline is more favorable to the formation of π-complex than azobenzene in terms of the ground-state conformation of the molecules.

The last step of the reaction (i.e. the loss of HOAc and the formation of cyclomercurated products) is probably the rate-determining step, based on solvent effects. Further studies on the mechanism are still in progress.[16] In the cases of **3a**, **10a**, and **32a**–**36a**, formation of the para-mercurated products is possible through an uncomplexed mechanism.

Conclusions

The mercuration of Schiff bases of 36 substituted benzylideneanilines studied to date gives different results than those reported by Singh et al.[5] Characterization of the structures of the products by IR, ^{1}H NMR, ^{13}C NMR, and MS indicates that for all of the reactions, the mercury is directed to the ortho position of the *N*-phenyl ring or the para position of the *N*-phenyl ring when it is not occupied by a substituent.

The position of the HgCl group in compound **7b** is confirmed by a single-crystal molecular structure determination, which also provided circumstantial evidence for the existence of an N→Hg intramolecular coordination bond with a four-membered ring in the Schiff base type arylmercury compound. On the basis of this structural information and the relevant literature a probable mechanism is proposed, in which the mercuration at the ortho position of the *N*-phenyl ring is facilitated by the imino moiety which forms a coordination complex with $Hg(OAc)_2$ in the first step, followed by a subsequent electrophilic substitution at the ortho position of the *N*-phenyl ring. This reaction is different from the metalation of benzylideneaniline by transition metals, in which the metal atom is usually directed to the ortho position of a *C*-phenyl ring,[1] and provides a new example for the so-called "cyclometalation" reaction.

Experimental Section

All reactions were performed in reagent grade solvents. The substituted benzylideneanilines were prepared following a standard procedure as described in the literature.[17] Melting points were measured on a WC-1 apparatus and are uncorrected. Elemental analyses were determined with a Carlo-Erba 1106. ^{1}H NMR and ^{13}C NMR were recorded on a Varian XL-200 or Bruker AC-80 and are referenced to the residual solvent resonance (DMSO-d_6, ^{1}H NMR at 2.60 ppm and ^{13}C NMR at 39.7 ppm). Infrared spectra were recorded on a Perkin-Elemer FT-1750 spectrometer. EI mass spectra were obtained on a VG-ZAB-HS spectrometer, operated at 20 or 70 eV with a source temperature of ca. 230 °C. Samples were introduced by means of a direct insertion probe. DAT and TG were measured on a RIGAKU thermal analyzer.

General Procedure for the Workup of the Mercuration Reaction. In a round-bottom flask equipped with a condenser, was placed equal amounts (moles) of the Schiff base and mercuric acetate (enough reagent grade methanol was added to make the concentration of the Schiff base ~0.1 M). A typical run is 1.25 g (5 mmol) of *N*-(4-nitrobenzylidene)-4-toluidine (**1a**), 1.6 g (5 mmol) of mercuric acetate, and 50 mL of methanol. This mixture was stirred and refluxed for 4 h. At the end of the reaction, the mixture was allowed to cool down to room temperature, the lithium chloride (typically 0.50 g or 12 mmol dissolved in hot methanol) was added, and the resulting thick mixture was stirred for about 10 min. The resulting precipitate was filtered off, washed with ether, and dried in vacuo. Crystallization from chloroform or other solvents gave crystals of the corresponding mercurated derivatives. The compounds prepared by this procedure are as follows.

2-(Chloromercurio)-*N*-(4-nitrobenzylidene)-4-toluidine (1b). The filtered precipitate was crystallized from chloroform to give 2.0 g (84%) of **1b** as yellow needles: mp 265.5–266.5 °C; ^{1}H MNR (200 MHz, DMSO-d_6) δ 9.00 (s, 1 H), 8.46 (d, 2 H, J = 8.6 Hz), 8.25 (d, 2 H, J = 8.2 Hz), 7.53 (s, 1 H), 7.50 (d, 1 H, J = 8.8 Hz), 7.28 (d, 1 H, J = 8.0 Hz), 2.41 (s, 3 H); ^{13}C NMR (50.3 MHz, DMSO-d_6) δ 156.7, 152.3, 150.7, 148.7, 141.7, 137.3, 136.5, 129.6, 129.2, 124.0, 116.9, 20.0; IR (KBr) 3046, 2913, 1625, 1597, 1574, 1515, 1467, 1339, 888, 856, 813, 750 cm^{-1}; EIMS (70 eV) [*m*/*e* (relative intensity)] 476 (M$^+$, 31.46), 327 (M − 149, 4.50), 239 (M − HgCl, 12.58). Anal. Calcd for $C_{14}H_{11}ClHgN_2O_2$: C, 35.37; H, 2.32; N, 5.89. Found: C, 35.17, H, 2.31; N, 5.64.

The selected physical and analytical data for the following compounds (**2b**–**37b**) are summarized in Table IV.

2-(Chloromercurio)-4-methoxy-*N*-(4-nitrobenzylidene)-aniline (2b). Crystallization of the filtered solid from chloroform gave **2b** as orange needles.

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[14] Kiefer, E. F.; Waters, W. L.; Calson, D. A. *J. Am. Chem. Soc.* **1968**, *90*, 5127–5131.

[15] Burgi, H. B.; Dunitz, J. D. *Helv. Chim. Acta* **1970**, *53*, 1747–1762.

[16] In order to further investigate the reaction mechanism we intend to carry out the kinetic measurements including the substituent effects, quantitative solvent effects, and deuterium isotope effects. These will be reported elsewhere.

[17] Vogel, A. I. *Practical Organic Chemistry*; Longmans: London, 1970; p 635.

Table IV. Selected Physical and Analytical Data for Compounds 2b–37b

			anal. calcd (found)			MS [m/e (M^+)]	
compd	yield (%)	mp (°C)	C	H	N	calcd	obsd
2b	63	264–266	34.22 (34.22)	2.24 (2.30)	5.70 (5.21)	492	492
3b	87	346–348	22.41 (22.50)	1.15 (1.41)	4.02 (3.79)	698	698
4b	85	338.5–339.5	31.48 (31.74)	1.62 (1.93)	5.65 (5.26)	496	496
5b[a]	93	343–344	30.82 (30.95)	2.05 (1.91)	4.79 (4.81)	540	540
6b	78	>350	26.57 (26.54)	1.36 (1.43)	4.77 (4.15)	588	588
7b[a]	90	272–273	41.06 (41.02)	2.70 (2.75)	5.04 (4.93)	512	512
8b	70	165–166	39.07 (38.96)	2.79 (2.80)	3.26 (3.08)	431	431
9b	54	187–188	37.67 (37.76)	2.69 (2.72)	3.14 (3.18)	447	447
10b	50	276.5–277.5	23.96 (23.60)	1.38 (1.79)	2.15 (1.91)	651	651
11b	44	210–211	34.63 (34.45)	2.00 (2.24)	3.11 (2.78)	451	451
12b	43	210–212	31.52 (31.19)	1.82 (1.60)	2.83 (2.53)	495	495
13b	74	219–221	28.78 (28.77)	1.66 (1.65)	2.58 (2.47)	543	543
14b		158–159	37.67 (37.76)	2.69 (2.98)	3.14 (2.85)	447	447
15b		174–176				507	507
16b	95	245–246.5	40.59 (40.50)	3.59 (3.58)	5.92 (5.81)	474	474
17b	87	184–186	39.13 (38.86)	3.04 (3.02)	3.04 (2.98)	461	461
18b	81	216–217	39.18 (38.93)	3.27 (3.27)	2.86 (2.73)	491	491
19b	91	226.5–228	39.13 (38.98)	3.04 (3.04)	3.04 (2.87)	461	461
20b	85	200–202	36.17 (35.88)	2.37 (2.39)	3.01 (3.21)	465	465
21b	93	>350	36.17 (36.16)	2.37 (2.29)	3.01 (2.98)	465	465
22b	94	220–222	36.17 (35.74)	2.37 (2.35)	3.01 (3.20)	465	465
23b	95	224–226	33.01 (32.72)	2.16 (2.15)	2.75 (2.78)	509	509
24b	80	208–210	33.01 (32.78)	2.16 (2.15)	2.75 (2.78)	509	509
25b	90	278–280	35.37 (35.17)	2.32 (2.29)	5.89 (5.86)	476	476
26b	86	240–241	35.37 (35.21)	2.32 (2.27)	5.89 (5.81)	476	476
27b	83	209–211	44.79 (44.61)	3.34 (3.30)	5.50 (5.35)	510	510
28b	75	170–172	44.76 (44.78)	4.51 (4.53)	2.18 (1.91)	645	645
29b	61	172–174	43.67 (43.63)	4.40 (4.43)	2.12 (2.18)	661	661
30b	66	189–191	41.57 (40.92)	3.92 (3.91)	2.11 (2.00)	665	665
31b	54	186–187	38.95 (38.81)	3.67 (3.73)	1.98 (1.94)	709	709
32b	90	202–204	39.07 (38.73)	2.79 (2.73)	3.26 (3.28)	431	431
33b	88	290–291	35.37 (35.34)	2.32 (2.31)	5.89 (5.88)	476	476
34b	85	219–220	27.94 (28.03)	2.07 (2.08)	3.62 (3.73)		*b*
35b[a]	86	297–299	24.32 (24.37)	1.62 (1.60)	3.78 (3.47)	698	698
36b	90	311–312	23.66 (23.94)	1.41 (1.55)	3.94 (4.10)		*b*
37b	52	254–256	33.84 (33.47)	1.95 (1.95)	6.07 (5.63)	462	462

[a] Contains 0.5 molecule of crystalline 1,4-dioxane. [b] No M^+ was found due to the weakness of the C–Hg bond, but M – HgOAc and M – HgCl were observed for **34b** and **36b**, respectively.

2,4-Bis(chloromercurio)-*N*-(4-nitrobenzylidene)aniline (3b). The crude product was crystallized from DMSO to give **3b** as yellow needles.

2-(Chloromercurio)-4-chloro-*N*-(4-nitrobenzylidene)aniline (4b). The filtered solid was crystallized from 1,4-dioxane to give **4b** as yellow needles.

2-(Chloromercurio)-4-bromo-*N*-(4-nitrobenzylidene)aniline (5b). The crude product was crystallized from 1,4-dioxane to yield yellow needles of **5b**$\cdot{}^{1}/_{2}\mathrm{C_4H_8O_2}$.

2-(Chloromercurio)-4-iodo-*N*-(4-nitrobenzylidene)aniline (6b). Crystallization from chloroform gave yellow crystals of **6b**.

α-(Chloromercurio)-*N*-(4-nitrobenzylidene)-β-naphthylamine (7b). The filtered solid was crystallized from 1,4-dioxane to give **7b**$\cdot{}^{1}/_{2}\mathrm{C_4H_8O_2}$ as yellow needles.

2-(Chloromercurio)-*N*-(benzylidene)-4-toluidine (8b). Crystallization from chloroform gave **8b** as white needles.

2-(Chloromercurio)-4-methoxy-*N*-(benzylidene)aniline (9b). The filtered solid was dissolved in hot chloroform and then the methanol was added dropwise until the white precipitate appeared. The mixture was heated again to make the precipitate dissolve. After cooling, white crystals of **9b** were obtained.

2,4-Bis(chloromercurio)-*N*-(benzylidene)aniline (10b). The filtered solid was crystallized from the mixture solvent of DMSO and methanol to give a white solid of **10b**.

2-(Chloromercurio)-4-chloro-*N*-(benzylidene)aniline (11b). Crystallization from chloroform gave white crystals of **11b**.

2-(Chloromercurio)-4-bromo-*N*-(benzylidene)aniline (12b). Crystallization from chloroform yielded white crystals of **12b**.

2-(Chloromercurio)-4-iodo-*N*-(benzylidene)aniline (13b). Crystallization from chloroform gave white needles of **13b**.

14b and **15b** were synthesized according to the literature method.[5]

2-(Chloromercurio)-*N*-(4-(dimethylamino)benzylidene)-4-toluidine (16b). Crystallization from dichloromethane gave yellow crystals of **16b**.

2-(Chloromercurio)-*N*-(4-methoxybenzylidene)-4-toluidine (17b). Crystallization from chloroform gave white crystals of **17b**.

2-(Chloromercurio)-*N*-(3,4-dimethoxybenzylidene)-4-toluidine (18b). Crystallization from 1,4-dioxane yielded white crystals of **18b**.

2-(Chloromercurio)-*N*-(2-methoxybenzylidene)-4-toluidine (19b). Crystallization from methanol gave white crystals of **19b**.

2-(Chloromercurio)-*N*-(4-chlorobenzylidene)-4-toluidine (20b). Crystallization from chloroform gave white crystals of **20b**.

2-(Chloromercurio)-*N*-(3-chlorobenzylidene)-4-toluidine (21b). Crystallization from 1,4-dioxane gave white crystals of **21b**.

2-(Chloromercurio)-*N*-(2-chlorobenzylidene)-4-toluidine (22b). Crystallization from methanol gave white crystals of **22b**.

2-(Chloromercurio)-*N*-(4-bromobenzylidene)-4-toluidine (23b). Crystallization from chloroform gave white crystals of **23b**.

2-(Chloromercurio)-*N*-(3-bromobenzylidene)-4-toluidine (24b). Crystallization from methanol gave white crystals of **24b**.

2-(Chloromercurio)-*N*-(3-nitrobenzylidene)-4-toluidine (25b). Crystallization from 1:1 dioxane/methanol gave pale yellow crystals of **25b**.

2-(Chloromercurio)-*N*-(2-nitrobenzylidene)-4-toluidine (26b). Crystallization from chloroform gave yellow crystals of **26b**.

α-(Chloromercurio)-(*N*-dimethylaminobenzylidene)-β-naphthylamine (27b). Crystallization from chloroform gave yellow crystals of **27b**.

Mercuration Reaction of 28a–31a. 4′-((Arylimino)methylbenzo-15-crown-5 (**28a–31a**) were prepared by treating 4′-(formylbenzo)-15-crown-5 with corresponding substituted anilines (1:1 molar ratio) in refluxing ethanol. Mp: for **28a** 104.5–105.5 °C; **29a** 102–103 °C; **30a** 104–105 °C; **31a** 123–125 °C. 4′-(Formylbenzo)-15-crown-5 was prepared according to the literature method.[18] Mp: 80–81 °C.

Mercuration of 28a. To a solution of **28a** (1.00 g, 2.6 mmol) in methanol was added 0.80 g of mercuric acetate (2.5 mmol); the mixture was refluxed for 4 h and allowed to cool to room temperature. The resulting white crystals were filtered off, washed with methanol, and dried in vacuo to give **28b**.

Compounds **29b–31b** were prepared by using the above method.

4-(Chloromercurio)-*N*-benzylidene-2-toluidine (32b). Crystallization of the filtered solid from methanol yielded white crystals of **32b**.

4-(Chloromercurio)-*N*-(nitrobenzylidene)-2-toluidine (33b). Crystallization of the filtered solid from 1,4-dioxane gave **33b** as yellow needles.

2,4-Bis(acetomercurio)-6-methoxy-*N*-(4-nitrobenzylidene)aniline (34b). Crystallization from methanol yielded orange crystals of **34b**.

2,4-Bis(chloromercurio)-*N*-(2-nitrobenzylidene)aniline (35b). Crystallization of the filtered solid from 1,4-dioxane gave yellow crystals of **35b**$\cdot{}^1/_2C_4H_8O_2$.

2,4-Bis(chloromercurio)-6-methyl-*N*-(2-nitrobenzylidene)aniline (36b). The filtered solid was recrystallized from 1,4-dioxane to give yellow needles of **36b**.

4-(Chloromercurio)-*N*-(4-nitrobenzylidene)aniline (37b). To a solution of **1a** (1.13 g, 5 mmol) and BTMAC (benzyltrimethylammonium chloride) (0.95 g, 5 mmol) in dry methanol (50 mL) was added 1.60 g (5 mmol) of mercuric acetate. The mixture was stirred and refluxed for 6 h, during which a yellow solid deposited. This solid was filtered off and dried in vacuo and then extracted with hot chloroform until the extracts were nearly colorless. Concentration of the extracts and subsequent crystallization gave yellow needles of **37b** as the main product. The remaining insoluble solid was recrystallized from DMSO to give yellow needles of **3b**.

X-ray Structure Determination of 7b. Single crystals of **7b** suitable for X-ray diffraction study were obtained by slow evaporation of the solution of **7b** in 1,4-dioxane at room temperature. A single crystal of approximate dimensions 0.2 × 0.2 × 0.25 mm was mounted on the end of a glass fiber. The X-ray diffraction intensity data of 3196 independent reflections, of which 2666 with $I > 3\sigma(I)$ were observable, were collected with an Enraf-Nonius CAD-4 diffractometer by using graphite monochromated Cu Kα radiation with the ω-2θ scan mode within the range of $2 \leqslant 2\theta \leqslant 120°$. The structure was solved by direct methods using the MULTAN82 program. The non-hydrogen atoms were found by difference Fourier (ΔF) synthesis and blocked diagonal matrix least-squares procedures. Hydrogen atoms were fixed by the theoretical method. After three cycles of refinement by full-matrix least-squares procedure with anisotropic thermal parameters for all non-hydrogen atoms, the final values of $R\ [=\sum||F_o| - |F_c||/|F_o|] = 0.073$ and $R_w\ \{=[\sum w(|F_o| - |F_c|)^2/\sum_w F_o^{\,2}]^{1/2}\} = 0.075$ were obtained.[19] An ORTEP drawing of **7b** is shown in Figure 1.

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Supplementary Material Available: A listing of spectral data for compounds **2b–37b**, figures showing the thermal analysis curve and molecular packing in the unit cell for **7b**, and tables of positional parameters and their estimated deviations for all non-hydrogen atoms, bond distances, bond angles, deviations of atoms from the mean plane, and crystal data and experimental details for the structure determination of **7b** (14 pages). Ordering information is given on any current masthead page.

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(18) Hyde, E. M.; Shaw, B. L.; Shepherd, I. *J. Chem. Soc., Dalton Trans.* 1978, 1696–1705.

(19) All crystallographic calculations were carried out on a PDP 11/44 computer with the CAD4-SDP program package (Enraf-Nonius, Delft, The Netherlands).

Synthesis and Photochemistry of the Aqueous-Soluble (η^5-$C_5H_4CH_2CH_2NH_3^+$)$_2$Mo$_2$(CO)$_6$ Complex. Generation of 19-Electron Complexes in Aqueous Solution

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The synthesis and photochemistry of the (η^5-$C_5H_4CH_2CH_2NH_3^+$)$_2$Mo$_2$(CO)$_6$ complex are described. The NO_3^- salt is soluble in aqueous solutions at pH 8 or lower; the PF_6^- salt was used in organic solvents. The photochemistry of the molecule is similar to the photochemistry of the $Cp_2Mo_2(CO)_6$ (Cp = η^5-C_5H_5) complex: irradiation into the low-energy tail of the lowest energy absorption band ($\lambda_{max} \approx 503$ nm; $d\pi \rightarrow \sigma^*$) results in homolytic cleavage of the Mo–Mo bond to form (η^5-$C_5H_4CH_2CH_2NH_3^+$)Mo(CO)$_3$ radicals. These 17-electron radicals can be trapped with chlorine atom donors (e.g., CCl_4 in nonaqueous solution or CCl_3CH_2OH in aqueous solution) to form (η^5-$C_5H_4CH_2CH_2NH_3^+$)Mo(CO)$_3$Cl. Irradiation of (η^5-$C_5H_4CH_2CH_2NH_3^+$)$_2$Mo$_2$(CO)$_6$ in the presence of ligands [e.g., phosphines in nonaqueous solution or water-soluble phosphines such as PTA (phosphatriazaadamantane) in aqueous solution] resulted in disproportionation of the dimer complex. The disproportionation reactivity is consistent with the intermediate formation of 19-electron adducts. Like their counterparts in nonaqueous solvents, the putative 19-electron adducts generated in aqueous solution are good reductants. They were used to reduce methylviologen and cytochrome *c* in aqueous solution. Reduction of protons to H_2 did not occur, and this led us to reexamine our earlier results in which we suggested that 19-electron complexes formed by irradiation of $(CpCOOH)_2W_2(CO)_6$ in basic aqueous solution reduced water to H_2. CO_2 is formed in a 1:1 ratio with H_2 in this reaction, and we propose the water-gas shift reaction is the source of the H_2.

We recently began a research program to explore the reactivity of 19-electron organometallic complexes in aqueous solution.[1–4] Nineteen-electron complexes have several features that make them ideal reducing agents,[8]

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