^{19}F NMR study of relative polarities and reactivities of N—H, N—Hg, and N—Au bonds in 2-(4-fluorophenyl)benzimidazole and its PhHg and Ph_3PAu derivatives in intermolecular exchange

A. S. Peregudov, L. N. Usatova, E. I. Smyslova, E. I. Fedin, and D. N. Kravtsov*

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085

It has been shown by the ^{19}F NMR method that the relative polarities of nitrogen—element bonds in 2-(4-fluorophenyl)benzimidazole and its PhHg and PPh_3Au derivatives increase in the order N—H < N—Hg < N—Au. Intermolecular exchange reactions of hydrogen—mercury, hydrogen—gold, and mercury—gold types in binary mixtures of these compounds have been studied by dynamic ^{19}F NMR. It has been found that these reactions occur by a bimolecular associative mechanism and that the N—H bond is substantially less reactive than the N—Hg and N—Au bonds, which have identical reactivities within the limits of sensitivity of the method used.

Key words: bond polarity, ^{19}F NMR, exchange reactions, kinetics and mechanism, 2-(4-fluorophenyl)benzimidazole, PhHg and Ph_3PAu derivatives.

In recent years we have studied polarity and reactivity in the exchange of σ-bonds formed by various elements with hydrogen atoms or univalent groups of the L_nM type, where M is an atom of a heavy transition or nontransition metal, in HX acids and their L_nM-derivatives.[1,2] Five-membered N-heterocyclic compounds and their L_nM-derivatives are an interesting class of the above-mentioned compounds, since substances with a heterocyclic moiety, in particular, with an imidazole moiety are often found in plants and animals and play an important biological role, since they exhibit strong physiological effects.[3] Heterocyclic derivatives of heavy metals that are hazardous for living organisms, in particular, organomercury derivatives, can arise in them by biological alkylation[4] and subsequent exchange reactions of hydrogen—mercury type. Therefore, a study of relative stabilities and reactivities of metal—element and hydrogen—element bonds in type (1) and (2) exchange reactions and of mechanisms of the corresponding reactions is urgent from the biological viewpoint. Note also that gold derivatives are not toxic and find application in therapy.[5]

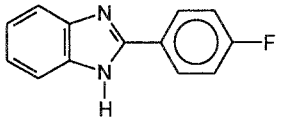
$$H—X + L_nM—Y \rightleftharpoons H—Y + L_nM—X \quad (1)$$

$$L_nM^1—X + L_nM^2—Y \rightleftharpoons L_nM^1—Y + L_nM^2—X \quad (2)$$

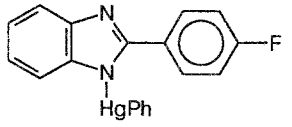
Imidazole type systems are also of interest from the theoretical viewpoint, since both these compounds themselves and their organometallic derivatives are potential tautomeric systems in which migration processes, unlike those in systems with closely arranged centers, for example in pyrazole type systems,[6] should occur by an intermolecular exchange mechanism.

We used 2-(4-fluorophenyl)benzimidazole (**1**) and its NHgPh (**2**) and $NAuPPh_3$ (**3**) derivatives as model compounds for investigating the properties of N—H and N—ML_n bonds in heterocyclic systems.

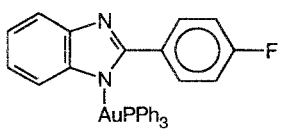
These compounds have been chosen, first, due to the synthetic accessibility of the starting heterocyclic compound. In addition, convenient methods for the synthesis of the Ph_3PAu derivative of 2-phenylbenzimidazole and benzimidazole[7,8] and the PhHg derivative of 2-phenylbenzimidazole[9] have been developed previously. Furthermore, the presence of the indicator 4-fluorophenyl group in compounds **1**—**3** makes it possible to study relative polarities of N—Q bonds by determining



1



2



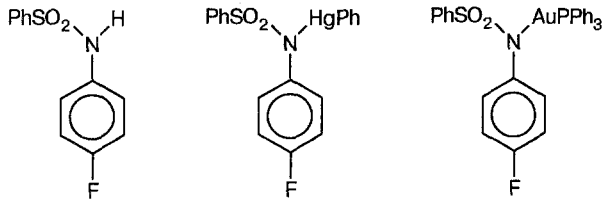
3

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1574—1580, August, 1995.

1066-5285/95/4408-1513$12.50

the fluorine chemical shifts (FCS)[1] and also to use dynamic ^{19}F NMR to study intermolecular exchange, which belongs to simple two-center type under the conditions of proton decoupling. Finally, a comparison of the properties of N—Au and N—Hg bonds is of particular interest, since the Ph_3PAu and PhHg groups are isoelectronic.

The relative polarities of the N—H, N—HgPh, and N—$AuPPh_3$ bonds have been studied previously using 4′-fluorobenzenesulfonanilide (**4**) and its PhHg (**5**) and Ph_3PAu derivatives (**6**) as examples.[10,11]



4 **5** **6**

It should be noted that in the case of compound **5**, the results may be affected to a certain extent by the possible intramolecular coordination of the PhHg group to the oxygen atom of the SO_2 group, which exists, according to X-ray diffraction analysis,[12] in PhHg derivatives of 2′-substituted benzenesulfonanilides.

A. S. Peregudov *et al.*[11] showed at a semiquantitative level without detailed investigation of the kinetics of exchange reactions of the hydrogen—mercury (3) or hydrogen—gold (4) types that at 25 °C in a DMSO solution, the N—Hg bond is more reactive than the N—Au bond.

$$RR^1N{-}H + RR^1N^*{-}HgPh \rightleftharpoons RR^1N{-}HgPh + RR^1N^*{-}H \quad (3)$$

$$RR^1N{-}H + RR^1N^*{-}AuPPh_3 \rightleftharpoons RR^1N{-}AuPPh_3 + RR^1N^*{-}H \quad (4)$$

$R = PhSO_2$, $R^* = 4\text{-}FC_6H_4$

It should be noted that from the kinetic viewpoint, reactions (1) and (2) have been studied rather extensively for systems incorporating nontransition metals.[13] Quantitative data on the kinetics of reactions (2) involving transition metals are very scarce.[14] Information on the kinetics of reactions (1) involving transition metals is missing from the literature. Type (1) and (2) exchange reactions in heterocyclic systems have not been studied for transition or nontransition metals.

Results and Discussion

Table 1 presents the FCS values for compounds **1**—**3** in DMSO and pyridine. In relatively inert media, these compounds are insoluble. At 25 °C, the values of FCS practically do not depend on the concentration over the 0.1—0.005 *M* range, which indicates that there is no noticeable association of these compounds under these conditions. The data of Table 1 indicate that the electron-withdrawing effect of the 2-benzimidazole group increases in the order:

Table 1. FCS values for 0.05 *M* solutions of compounds **1**—**3** (ppm, relative to fluorobenzene)

Compound	Solvent	CSF
1	Pyridine	−2.56
	DMSO	−1.32
2	Pyridine	−1.07
	DMSO	−0.96
3	Pyridine	−0.58
	DMSO	0.38

$$Ph_3PAu < PhHg < H.$$

Thus, according to the previously reported considerations,[1] polarity of the nitrogen—element bond, *i.e.*, $N^{\delta-}{-}Q^{\delta+}$, increases according to sequence (5), which is similar to that found for compounds **4**—**6**.

$$N{-}H < N{-}HgPh < N{-}AuPh_3 \quad (5)$$

Therefore, the sequence in which relative polarities of the nitrogen—element bonds vary does not depend on the type of the starting NH acid, at least, for the acids under consideration, whose acidities in DMSO differ by almost 4 orders of magnitude (**4**, pK_a = 12.4,[15] 2-phenylbenzimidazole, pK_a = 16.2 [16]).

It should be taken into account that the N—H and N—Hg bonds are additionally polarized in pyridine or DMSO due to the formation of H-bonds or coordination of the mercury atom to a solvent molecule, respectively. This is indicated by the substantial increase in the shielding of fluorine in compounds **4** and **5** on going from solutions in PhCl to solutions in pyridine or DMSO and also the absence of the above-mentioned effect for the benzyl analog, *N*-benzyl-4′-fluorobenzenesulfonanilide.[17,18]

An analysis of the distinctions in the variation of shielding of the fluorine nuclei on going from an NH acid to its organometallic derivatives [$\Delta FCS = FCS(L_nM) - FCS(H)$] (Table 2) leads to the following results. In the case when $L_nM = Ph_3PAu$, the FCS values for imidazole type systems are lower than those for sulfonamide type systems, as might be expected, since the bridging fragment increases by an sp^2-hybridized carbon atom on going from compound **4** to compound **1**. At the same time, for the systems where L_nM = PhHg, the ΔFCS value increases on going from **4** to **1**, which is especially clear-cut in pyridine.

Phenomenologically, this may be associated with the fact that the difference between the polarities of the

Table 2. Values of ΔFCF = [FCS(L_nM) − FCS(H)] (ppm) for compounds **1**—**6**

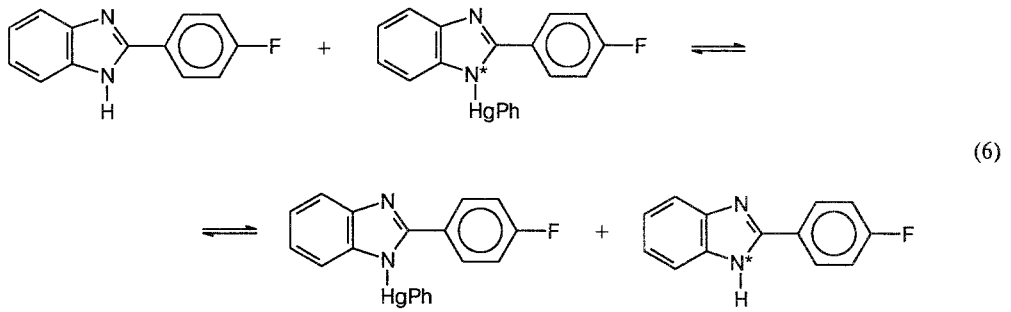
L_nM	Starting NH acid			
	1		**4**	
	Pyridine	DMSO	Pyridine	DMSO
Ph_3PAu	1.98	1.70	2.71	2.33
PhHg	1.49	0.36	0.92	1.28

N—Hg and N—H bonds in the benzimidazole system is greater than that in the sulfonanilide system.

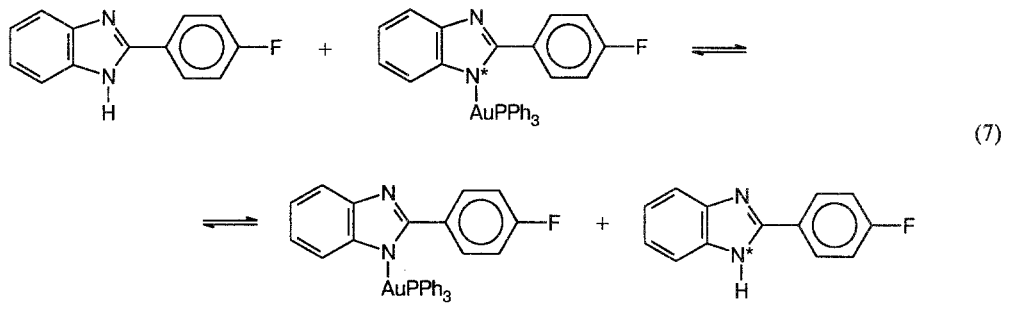
The difference observed between the polarities of the N—Hg and N—H bonds in compounds **1** and **2** compared with compounds **4** and **5** may be caused by the above-mentioned intramolecular coordination in compound **5**. In fact, the change in the shielding of fluorine on going from compound **1** to **2** results only from the replacement of the less polar N—H bond by the more polar N—Hg bond and from the increase in the electron density on the indicator 4′-fluorophenyl group. In contrast, for a similar reason, the increase in the electron density at the fluorine atom on going from **4** to **5** may be partly balanced due to the decrease in the electron density at the nitrogen atom resulting from the effect of intramolecular coodination between the Hg atom and the O atom and due to the increase in the electron-withdrawing ability of the $PhSO_2$ group.

In the first approximation, relative polarities of bonds should govern their labilities.[19] In order to verify whether there is a parallel variation of this sort in the case of N—H and N—M bonds, we studied degenerate exchange of the hydrogen—mercury (6), hydrogen—gold (7), and mercury—hydrogen (8) types in pyridine by dynamic ^{19}F NMR.

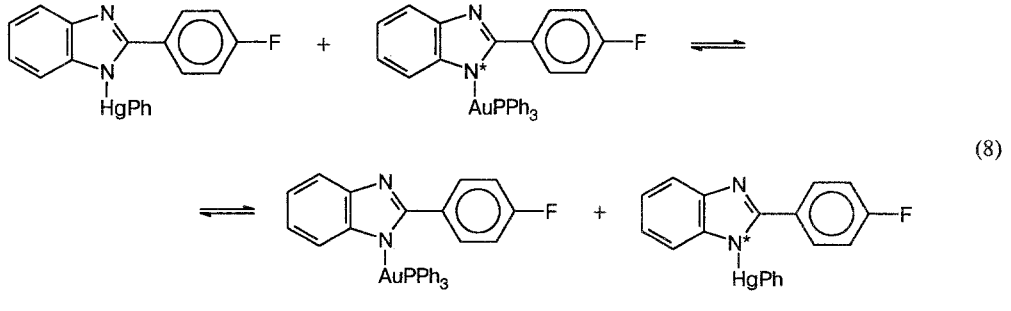
Under certain conditions all three of these reactions occur at rates comparable to the ^{19}F NMR time scale. The conditions for slow exchange under which the spectrum exhibits two relatively narrow signals of fluorine, whose positions correspond to those of the signals



(6)

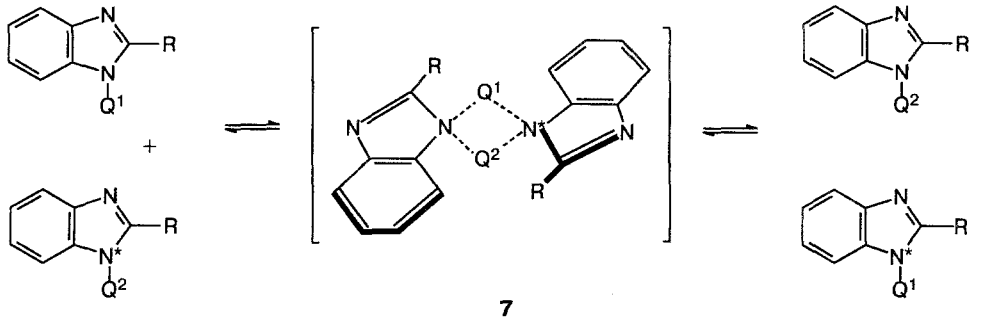


(7)



(8)

Scheme 1



7

R = 4-FC_6H_4

of individual compounds, are realized at −50 °C. However, in hydrogen—metal systems of types (6) and (7), this occurs at rather high concentrations (~0.1—0.05 *M*), while in the case of reaction (8), this requires a high degree of dilution (~0.01 *M*) due to high rates of exchange and a substantially smaller difference in the shielding of the fluorine nuclei in the individual compounds. Therefore, the orders of reaction (8) with respect to each component were determined at −43 °C, rather than at ambient temperature, as was done for reactions (6) and (7) (Table 3). In general, the exchange reactions studied are approximately of the first order with respect to each of the reactants. An increase in temperature results in coalescence of the signals of the two indicator fluorine nuclei into a singlet with an averaged FCS value. The temperatures of coalescence are given in Table 3.

Based on the analysis of the full shapes of lines in the temperature- and concentration-dependent ^{19}F NMR spectra of mixtures (6)—(8) we determined the effective lifetimes of the exchanging species and evaluated the rate constants and activation parameters of the reactions (see Table 3). From the data of this Table, one can see that these reactions are characterized by low activation enthalpies and high negative values of activation entropies, which indicates that they occur by a bimolecular association mechanism (Scheme 1).

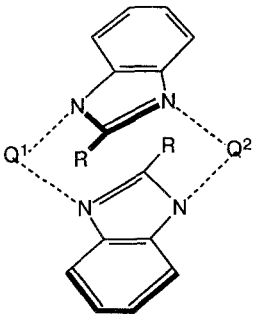
A similar mechanism has been suggested for exchanges of the hydrogen—mercury (3) mercury—mercury (9) types.[20]

$$RR^1N{-}HgPh + RR^1N^*{-}{}^*HgPh \rightleftharpoons$$

$$\rightleftharpoons RR^1N{-}{}^*HgPh + RR^1N^*{-}HgPh \qquad (9)$$

R = Me, $R^1 = PhSO_2$

It should also be noted that in principle reactions (6)—(8) might occur by a mechanism of the type of intermolecular tautomerism involving the formation of more complex eight-membered transition states (**8**),



8 R = 4-FC_6H_4

Table 3. Kinetic and activation parameters of exchange reactions (6)—(8) in pyridine

Reaction	C^a /mol L^{-1}	m	n^b	T/°C[c]	$k_{298} \cdot 10^3$ /L mol^{-1} s^{-1}	$\Delta H^{\neq}$ /kcal mol^{-1}	$\Delta S^{\neq}$ /cal deg^{-1} mol^{-1}	$\Delta G^{\neq}_{298}$ /kcal mol^{-1}
		(T/°C)						
(6)	0.059	1.1±0.2	1.2±0.2 (25)	65	5.1±3.1	3.4±0.7	−30.1±1.2	12.4±0.3
(7)	0.100	1.0±0.2	1.0±0.2 (25)	39	2.5±1.3	4.0±1.0	−29.5±1.5	12.8±0.6
(8)	0.010	1.07±0.05	1.37±0.05 (−43)	2	88±45	5.0±0.7	−18.9±1.4	10.7±0.3

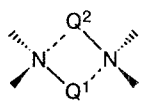
[a] The concentration of each of the starting reactants for the particular kinetic measurements. [b] m and n are the orders of the reaction with respect to X and Y, respectively, determined at the temperature given in parentheses. [c] The temperature of the coalescence.

rather than four-membered transition states (**7**). In this case, migrating species Q^1 and Q^2 would be located between two parallel planes of the ligands and simultaneously bound to the N(1) atom of "their own" benzimidazole fragment and to the N(3) atom of the other benzimidazole fragment.

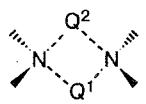
The rate constants of reactions (6)—(8) at 298 K, with allowance for the rather large errors in their determination, which are mostly due to errors of ±0.2 units in determining the reaction orders, indicate that the reaction rate increases on going from hydrogen—metal type exchanges to the mercury—gold type exchange. Thus, the reactivities of the N—Q bonds vary in the following sequence:

$$N—H < N—Hg \approx N—Au. \qquad (10)$$

While comparing this result with sequence (5) in which the relative polarities of the N—Q bonds vary, it should be noted that the N—H bond, which is less polar than the N—M bonds, proves to be also less reactive. Conversely, the N—Hg and N—Au bonds, which are characterized by different polarities, exhibit identical reactivities within the limits of the sensitivity of the method used. At the same time, a larger polarity of an N—Q bond should facilitate the formation of cyclic associates like **9**, which precede cyclic transition state **10** with completely delocalized bonds.[13]



9



10

Since the structures of the highest occupied electron shells of the metal atoms in PhHgX and Ph_3PAuX are identical, rings **9** and **10** incorporating mercury or gold should be characterized by identical degrees of the compatibility of the optimal geometry (sp^2 or sp + p) of the coordinated state of the metal atom. Therefore, one of the possible reasons why, as has been mentioned above, there is no parallel variation of the polarities of the N—Hg and N—Au bonds and their relative reactivities may be the fact that the Ph_3P ligand at the gold atom is larger than the Ph group at the mercury atom. This may result in steric restrictions to the formation of cyclic transition states like both **7**, in which the two bulky 2-(4-fluorophenyl)benzimidazole fragments must be located in one plane, and **8**. Thus, the steric factor can partly balance the effect of the greater polarity of the N—Au bond compared to the N—Hg bond. The foregoing is supported by the fact that the systems incorporating the Ph_3PAu group are characterized by lower negative values of the activation energy. This is especially pronounced for the mercury—gold system.

The above-discussed exchange reactions have been studied in pyridine solutions. Therefore, one should take into account that the reactivities of the N—H and N—Hg bonds might be substantially affected by the formation of H...N H-bonds and Hg...N coordinative bonds with pyridine molecules. In the case of compounds **4** and **5**, the occurrence of these bonds is indicated[10] by ^{19}F NMR data. The question whether the Ph_3PAu group forms an Au...N coordinative bond with a pyridine molecule remains open.[10] For example, it has been found previously that transition from chloroform to pyridine accelerates the exchange involving the N—H bonds in *N*-methylbenzenesulfonamide, but decelerates the exchange involving the N—Hg bond in its PhHg derivatives.[20]

Experimental

^{19}F–{^{1}H} NMR spectra were recorded on a Bruker WP-200 SY spectrometer operating at 188.31 MHz for fluorine. The values of FCS were determined by the method of replacement with respect to a solution of fluorobenzene in a given solvent. Positive FCS values correspond to an increase in the shielding of fluorine nuclei. The error of the determination of FCS was no more than ±0.02 ppm. Resonance conditions were stabilized using the deuterium signal from deuteromethanol placed between the wall of a 5-mm ampule and the wall of a 4-mm inserted tube containing a solution of a sample or a solution of a reference sample. The temperature was controlled with an accuracy of ±1 °C.

The effective lifetimes τ of exchanging species were determined by visual comparison of the experimental spectra with the theoretical spectra obtained by computer analysis of the full shapes of lines for two-center exchange with various populations and various widths of the signals of the starting compounds.[21]

The separation of the signals in the absence of the exchange exhibits an essential linear temperature dependence (with a correlation coefficient of 0.99) that may have either a positive [$\Delta\delta^\circ = 0.507T + 260.8$ (H + $AuPPh_3$); $\Delta\delta^\circ = 0.872T - 150.3$ (HgPh + $AuPPh_3$)] or a negative [$\Delta\delta^\circ = -0.671T + 483.4$ (H + HgPh)] slope. The values of $\Delta\delta^\circ$ near the coalescence were determined by extrapolation from the low-temperature values.

The orders of the reaction with respect to each of the components were evaluated from the expressions:[22]

$$1/\tau(A) = k[A]^{m-1}[B]^n;\ 1/\tau(B) = k[A]^m[B]^{n-1},$$

where the lifetimes of the exchanging species in each state τ(A) and τ(B) are related to the effective lifetime τ by the following ratios: $\tau(A) = \tau/P(B)$; $\tau(B) = \tau/P(A)$ [$P(A)$ and $P(B)$ are the populations of states A and B]. The ranges in which concentrations varied were 0.12—0.043 *M*, 0.17—0.046 *M*, and 0.1—0.013 *M* for reactions (6), (7), and (8), respectively.

The activation parameters were calculated by the standard procedure.[23] The data of dynamic NMR for reactions (6)—(8) at various temperatures are given in Table 4. The substantial error in determining the rate constant of the reaction is due to the errors in the reaction orders. The errors in determining $\Delta H^{\neq}$ by the standard least-squares method with a confidence probability of 95 % are no more than 0.01 kcal mol^{-1}. However, a detailed analysis of the errors in determining $\Delta G^{\neq}$, $\Delta H^{\neq}$, and $\Delta S^{\neq}$ by the method of Sandström,[23] taking into account not only the errors in determining *k*, but also the possible

Table 4. Effective lifetimes of exchanging species and rate constants of reactions (6)—(8) in pyridine obtained from analysis of the dynamic NMR spectra

Reaction	T/K	$\tau \cdot 10^{-3}$/s	$k \cdot 10^3/s^{-1}$ mol^{-1} L
(6) (H+Hg)*	338	1.8	11.0
	329	2.1	9.5
	320	2.4	8.3
	310	3.0	6.6
	301	3.6	5.5
	292	5.0	4.0
	283	5.6	3.6
	274	7.0	2.85
	265	8.8	2.3
(7) (H+Au)**	312	1.1	4.55
	308	1.5	3.2
	299	1.9	2.6
	289	2.5	2.0
	280	3.2	1.6
	271	4.1	1.2
	262	5.6	0.89
(8) (Hg+Au)***	302	1.8	110.0
	288	2.7	74.0
	275	5.0	63.0
	271	7.0	29.0
	266	8.0	25.0
	262	9.4	21.0
	257	11.0	18.0
	253	14.0	14.0
	243	18.0	11.0
	230	30.0	6.6

* The concentration of each component in the mixture was 0.059 M, the total order of reaction (6) $m+n$ = 2.3±0.2 (298 K). $\log k$ = (−0.8643±0.0006)(1/T) + (6.60±0.08); S = 0.019; r = −0.998. $\log(k/T)$ = (−0.7345±0.0006)(1/T) + (3.69±0.08); S = 0.019; r = −0.996.

** The concentration of each component in the mixture was 0.1 M, the total order of reaction (7) $m+n$ = 2.0±0.2 (298 K). $\log k$ = (−0.9998±0.0007)(1/T) +(6.76±0.09); S = 0.014; r = −0.998. $\log(k/T)$ = (−0.8749±0.0006)(1/T) + (3.87±0.08); S = 0.013; r = −0.998.

*** The concentration of each component in the mixture was 0.01 M, the total order of reaction (8) $m+n$ = 2.4±0.1 (230 K). $\log k$ = (−1.225±0.007)(1/T) + (9.06±0.31); S = 0.073; r = −0.982. $\log(k/T)$ = (−1.110±0.006)(1/T) + (6.20±0.30); S = 0.072; r = −0.980.

effect of the insufficiently wide temperature range of kinetic measurements (ΔT = 73, 50, 72 °C), showed that the errors can be considerably greater. The relevant data are presented in Table 3.

Pyridine and DMSO were purified by distillation over alkali, kept over freshly calcined molecular sieves, and once again distilled just prior to use. It was shown in special runs that the addition of water to the samples under study in pyridine has no effect on the kinetics of reactions (6)—(8) and the spectral pattern is completely reproducible with respect to samples and the temperature.

The known benzimidazole **1** was synthesized by the reaction of *o*-phenylenediamine with 4-fluorobenzoic acid and was identified by its melting point (258—259 °C, *cf.* Ref. 24: m.p. 257 °C). PhHg and Ph_3PAu derivatives **2** and **3** were prepared by the reaction of **1** with PhHgOH or Ph_3PAuCl, respectively, according to the known procedure[9] or the modified procedure.[8]

***N*-Phenylmercury-2-(4-fluorophenyl)benzimidazole (2).** An ethanolic solution of PhHgOH (0.7 g, 2.5 mmol) was added to a solution of 2-(4-fluorophenyl)benzimidazole (**1**) (0.53 g, 2.5 mmol) in the minimum quantity of ethanol. The resulting precipitate was recrystallized from ethanol to give **2** as a white crystalline solid, m.p. 248—249 °C. Found (%): C, 46.52; H, 2.74; N, 5.44; F, 3.87. $C_{19}H_{13}FHgN_2$. Calculated (%): C, 46.66; H, 2.66; N, 5.73; F, 3.88.

***N*-Triphenylphosphinegold-2-(4-fluorophenyl)benzimidazole (3).** NaH (0.02 g) was added to a stirred solution of 2-(4-fluorophenyl)benzimidazole (**1**) (0.2 g, 1.1 mmol) in 40 mL of anhydrous THF. After 20 min, Ph_3PAuCl (0.5 g, 1.0 mmol) was added and after 2.5 h the reaction mixture was filtered, the solvent was removed *in vacuo*, and the residue was dissolved in the minimum quantity of acetone. The solution was filtered, and 0.42 g (60 %) of compound **3** was precipitated by an ether—hexane (1 : 2) mixture as a white crystalline compound, m.p. 187—189 °C. Found (%): C, 55.47; H, 3.40; F, 2.51; N, 4.42; P, 4.56. $C_{31}H_{23}AuFN_2P$. Calculated (%): C, 55.53; H, 3.46; F, 2.83; N, 4.17; P, 4.62.

This work was carried out with financial support from the Russian Foundation for Basic Research (Project No. 93-03-5528).

References

1. D. N. Kravtsov, *Metalloorg. Khim.*, 1990, **2**, 157 [*Organomet. Chem. USSR*, 1990, **2** (Engl. Transl.)].
2. A. S. Peregudov, *Metalloorg. Khim.*, 1991, **5**, 120 [*Organomet. Chem. USSR*, 1991, **5** (Engl. Transl.)].
3. A. R. Katritsky, *Usp. Khim.*, 1972, **41**, 700 [*Russ. Chem. Rev.*, 1972, **41** (Engl. Transl.)].
4. J. S. Thayr, *J. Organomet. Chem.*, 1974, **76**, 265.
5. R. J. Puddephatt, *The Chemistry of Gold*, A, 1978, 247.
6. D. N. Kravtsov, L. A. Fedorov, A. S. Peregudov, and A. N. Nesmeyanov, *Dokl. Akad. Nauk SSSR*, 1971, **196**, 110 [*Dokl. Chem.*, 1971, **196** (Engl. Transl.)].
7. F. Bonati, M. Felini, B. R. Pietroni, and A. Burini, *Gazzetta Chim. Ital.*, 1982, **112**, 5.
8. F. Bonati, A. Burini, M. Felini, and B. R. Pietroni, *Gazzetta Chim. Ital.*, 1983, **113**, 105.
9. D. N. Kravtsov and A. N. Nesmeyanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1967, 1741 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1967, **16** (Engl. Transl.)].
10. A. S. Peregudov, E. G. Perevalova, E. I. Smyslova, and D. N. Kravtsov, *Metalloorg. Khim.*, 1988, **1**, 1402 [*Organomet. Chem. USSR*, 1988, **1** (Engl. Transl.)].
11. A. S. Peregudov, E. I. Smyslova, E. I. Fedin, and D. N. Kravtsov, *Metalloorg. Khim.*, 1990, **3**, 24 [*Organomet. Chem. USSR*, 1990, **3** (Engl. Transl.)].
12. L. G. Kuz'mina, N. G. Bokii, Yu. T. Struchkov, D. N. Kravtsov, and A. S. Peregudov, *Zh. Strukt. Khim.*, 1976, **17**, 333 [*J. Struct. Chem.*, 1976, **17** (Engl. Transl.)].
13. L. A. Fedorov, A. S. Peregudov, and D. N. Kravtsov, *Usp. Khim.*, 1979, **48**, 993 [*Russ. Chem. Rev.*, 1979, **48** (Engl. Transl.)].
14. P. E. Garrou, *Advances in Organomet. Chem.*, 1984, **23**, 95.

15. D. N. Kravtsov, A. S. Peregudov, E. S. Petrov, M. I. Terekhova, and A. I. Shatenshtein, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 1259 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1981, **30**, 993 (Engl. Transl.)].
16. M. I. Terekhova, E. S. Petrov, E. M. Rokhlina, D. N. Kravtsov, and A. I. Shatenshtein, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 1104 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1979, **28** (Engl. Transl.)].
17. A. N. Nesmeyanov, S. I. Pombrik, E. V. Polunkin, A. S. Peregudov, L. S. Golovchenko, D. N. Kravtsov, and E. I. Fedin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 763 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1981, **30**, 548 (Engl. Transl.)].
18. S. I. Pombrik, E. V. Polunkin, A. S. Peregudov, E. I. Fedin, and D. N. Kravtsov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 1289 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1982, **31**, 1148 (Engl. Transl.)].
19. J. D. Roberts and M. C. Caserio, in *Basic Principles of Organic Chemistry*, W. A. Benjamin Inc., New York—Amsterdam, 1964, Ch. 2.
20. L. A. Fedorov, A. S. Peregudov, and D. N. Kravtsov, *J. Organomet. Chem.*, 1972, **40**, 251.
21. I. I. Arnold, *Phys. Rev.*, 1956, **102**, 136.
22. B. I. Ionin, B. A. Ershov, and A. I. Kol'tsov, *YaMR spektroskopiya v organicheskoi khimii* [*NMR Spectroscopy in Organic Chemistry*], Khimiya, Leningrad, 1983, 252 pp. (in Russian).
23. J. Sandström, *Dynamic NMR Spectroscopy*, Academic Press, New York, 1982.
24. G. Sandera, R. W. Isensee, and L. Joseph, *J. Am. Chem. Soc.*, 1954, **76**, 5173.

Received December 29, 1993;
in revised form December 19, 1994