In separate experiments using similar quantities of the same starting materials and the same procedures, a 17% yield of $Co_2(CO)_8$ was obtained after 1.7 h and 95 atm and 20 °C and a 47% yield of $Co_2(CO)_8$ after 16 h at 95 atm and 107 °C.

Method 2. In a separate preparation, 0.441 g (63.54 mmol) of lithium, 6.881 g (53.69 mmol) of naphthalene, and 4.018 g (30.95 mmol) of cobalt chloride were placed in a 100-mL flask and 50 mL of diglyme was added to the mixture at −35 °C. After stirring overnight at that temperature there was little evidence of reaction. It was necessary to stir the mixture at −20 °C for an additional 72 h. When the gray-black slurry was then transferred to a centrifuge tube as previously described (vide supra), a scrap of unreacted lithium (0.060 g, 8.62 mmol) was recovered from the reaction flask.

The cobalt powder was washed by centrifugation with six 30-mL portions of hexanes and loaded into the stirred bomb with 150 mL of hexanes. The bomb was pressurized with carbon monoxide to 95 atm and allowed to stir overnight. In this experiment, the pressure drop with time was not monitored as closely as in the preceding experiment. After 8 h the theoretical pressure drop was observed. Heating to 100 °C overnight and cooling to room temperature failed to cause an appreciable change in the pressure of the remaining carbon monoxide. The bomb was then vented and the contents filtered to give a clear brown solution from which 3.856 g of $Co_2(CO)_8$ were isolated by concentration of the solution in vacuo. The yield, based on cobalt chloride, was therefore 73%.

Method 3. Lithium (0.506 g, 72.85 mmol), 9.138 g (71.39 mmol) of naphthalene, and 4.608 g (35.49 mmol) of cobalt chloride were placed in a 250-mL flask. Glyme (140 mL) was added to this mixture and the resulting slurry allowed to stir at −22 °C for 3 days. The gray-black product slurry was centrifuged and washed with hexanes at room temperature as described previously and placed in a stirred bomb with 300 mL of hexanes. After treatment with 95 atm of carbon monoxide for 4 days at 100 °C, a brown solution was obtained which when concentrated to small volume gave 3.400 g (56%) of orange-red $Co_2(CO)_8$.

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Registry No. $Co_2(CO)_8$, 10210-68-1; CO, 630-08-0; cobalt chloride, 7646-79-9; cobalt iodide, 15238-00-3; lithium naphthalide, 27939-69-1; cobalt, 7440-48-4.

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Exchange of Cyclopalladated Ligands in Chloro-Bridged Palladium(II) Complexes

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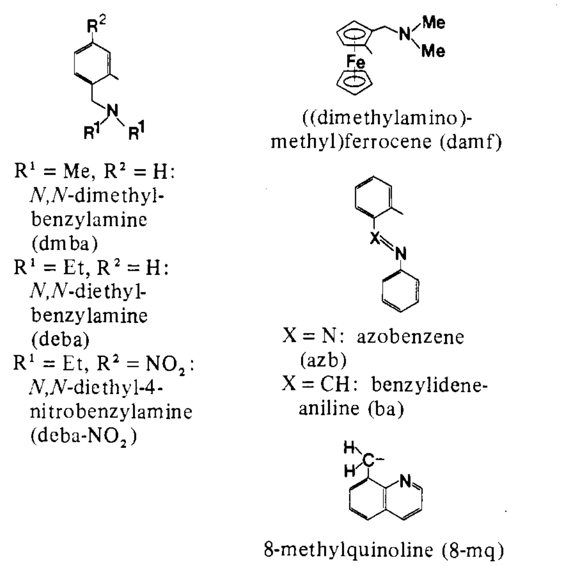
Cyclometalated complexes of transition metals have been intensively studied and a variety of their reactions reported.[1] In particular two types of substitution reactions are known, namely the exchange or substitution of ancillary nonmetalated ligands[1] and transmetalation reactions between cyclometalated complexes and free metal salts forming new metallocycles.[2] We report here a novel ligand-exchange reaction between a cyclopalladated complex and a free ligand to afford a new metallocycle. We have recently obtained evidence[3] that such a reaction could occur in the case of ortho-palladated *N,N*-dialkylbenzylamines in acetic acid solvent.

Chart I



R^1 = Me, R^2 = H: *N,N*-dimethylbenzylamine (dmba)
R^1 = Et, R^2 = H: *N,N*-diethylbenzylamine (deba)
R^1 = Et, R^2 = NO_2: *N,N*-diethyl-4-nitrobenzylamine (deba-NO_2)

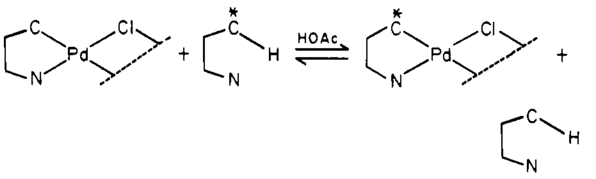
((dimethylamino)methyl)ferrocene (damf)

X = N: azobenzene (azb)
X = CH: benzylideneaniline (ba)

8-methylquinoline (8-mq)

Results and Discussion

This work deals with reaction 1, employing the ligands listed in Chart I.



(1)

The results obtained are summarized in the Table I. Entries 1 and 2 show that $[Pd(dmba)Cl]_2$ reacts smoothly with azobenzene at 50 °C in binary acetic acid (HOAc)–benzene or chloroform mixtures affording excellent crystals of $[Pd(azb)Cl]_2$ in good yields. Other N donor ligands such as *N,N*-diethylbenzylamine, *N,N*-diethyl-4-nitrobenzylamine, benzylideneaniline, and 8-methylquinoline also undergo this ligand-exchange reaction, giving the respective chloro-bridged dimers, eq 2 and entries 4–6, Table I. On the other hand, a

$$^1/_2[Pd(dmba)Cl]_2 + deba \rightleftharpoons {}^1/_2[Pd(deba)Cl]_2 + dmba \qquad (2)$$

ligand with an O donor atom, namely acetanilide, which is known to form an ortho-palladated complex,[4] does not react, entry 7, Table I. No ligand exchange is observed without accetic acid as co-solvent, entries 8 and 9, Table I. Adding benzene or chloroform to a reaction mixture is necessary to increase solubility of the starting complexes. The low solubility of a majority of chloro-bridged cyclopalladated compounds restricts the number of those that can be tested in reaction 1. As a result, only $[Pd(dmba)Cl]_2$ (mentioned above) and $[Pd(damf)Cl]_2$ have been successfully used in the reaction, entries 10–12, Table I. The latter proceeds under milder conditions compared to the former.

The ligand exchange between $[Pd(dmba)Cl]_2$ and 8-methylquinoline has been used to confirm the reaction stoichiometry, entry 6, Table I. GLC analysis of the reaction products has shown the presence of 0.091 and 0.042 mmol of free dmba and 8-mq, respectively. This means that 0.11 mmol of the incoming ligand is consumed when 0.09 mmol of the initially metalated ligand is liberated, in accord with the metal to ligand 1:1 stoichiometry of reaction 1 (within experimental uncertainties).

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Table I. Exchange of Cyclometalated Ligands in Chloro-Bridged Palladium(II) Complexes[a]

entry	complex	ligand	time, h	solvent	product	yield, %
1	$[Pd(dmba)Cl]_2$	azb	11.5	HOAc/PhH	$[Pd(azb)Cl]_2$	59
2	$[Pd(dmba)Cl]_2$	azb	10	$HOAc/CHCl_3$	$[Pd(azb)Cl]_2$	67
3	$[Pd(dmba)Cl]_2$[b]	azb	12	$HOAc/CHCl_3$	$[Pd(azb)Cl]_2$	54
4	$[Pd(dmba)Cl]_2$	deba-NO_2	24	HOAc/PhH	$[Pd(deba\text{-}NO_2)Cl]_2$	46
5	$[Pd(dmba)Cl]_2$	ba	24	HOAc/PhH	$[Pd(ba)Cl]_2$	39
6	$[Pd(dmba)Cl]_2$	8-mq	24	$HOAc/CHCl_3$	$[Pd(8\text{-}mq)Cl]_2$	64
7	$[Pd(dmba)Cl]_2$	acetanilide	12	HOAc/PhH	...	
8	$[Pd(dmba)Cl]_2$	azb	12	PhH	...	
9	$[Pd(deba)Cl]_2$	azb	24	$CHCl_3/PhH$	...	
10	$[Pd(damf)Cl]_2$[c]	azb[d]	4	$HOAc/CHCl_3$	$[Pd(azb)Cl]_2$	68
11	$[Pd(damf)Cl]_2$[c]	azb[d]	6[e]	$HOAc/CHCl_3$	$[Pd(azb)Cl]_2$	72
12	$[Pd(damf)Cl]_2$[c]	ba[d]	5[e]	$HOAc/CHCl_3$	$[Pd(ba)Cl]_2$	31

[a] Conditions: 0.064 mmol of complex; 0.152 mmol of ligand; 3 mL of HOAc; 3 mL of organic solvent; 50 °C. [b] In the presence of 0.128 mmol of free dmba. [c] 0.050 mmol. [d] 0.120 mmol. [e] At 25 °C.

The reversibility of this process has been demonstrated by reaction 2. After thermostating equimolar amounts of the reactants at 50 °C for 24 h, the final reaction mixture was observed to contain cyclopalladated complexes $[Pd(dmba)Cl]_2$ and $[Pd(deba)Cl]_2$ in the ratios 1:2.0 and 1:2.9, starting from the left and right, respectively, of eq 2.

We emphasize that the present system is of interest not only as an example of ligand exchange in cyclopalladated complexes but also as a tool for palladation of inactive substrates. In particular, it has been reported[5] that Na_2PdCl_4 does not metalate nitro-substituted dialkylbenzylamines,[6] but reaction 1 provides a simple method for preparing $[Pd(deba\text{-}NO_2)Cl]_2$ in good yield, entry 4, Table I.

The simplest reaction mechanism could be a sequence of a reversible protonolysis of a starting complex by acetic acid followed by ortho palladation of an incoming ligand by liberated PdCl(OAc). However, two observations make this mechanism rather unprobable. First, the starting complex is stable under the conditions of entry 2, Table I. Second, the yield of $[Pd(azb)Cl]_2$ is not significantly lowered in the presence of a leaving ligand, entry 3, Table I. We suppose that the reaction may involve an attack of the incoming ligand on chloro bridges to give a monomeric complex,[1,7] followed by protonolysis of the Pd–C bond of the palladocycle. The subsequent palladation of the incoming ligand and dissociation of the leaving one would accomplish the mechanism.

Experimental Section

The preparation of cyclopalladated compounds $[Pd(dmba)Cl]_2$,[5] $[Pd(deba)Cl]_2$,[8] $[Pd(dmaf)Cl]_2$,[9] $[Pd(azb)Cl]_2$,[10] $[Pd(ba)Cl]_2$,[11] and $[Pd(8\text{-}mq)Cl]_2$[12] have been previously reported. The identity of these complexes with those obtained in the present study was confirmed by IR and ^1H NMR spectroscopy, the latter only for monomeric soluble products.

General Procedure for Ligand Exchange. A starting cyclopalladated chloro-bridged complex (0.050–0.064 mmol) and an incoming ligand (0.120–0.152 mmol) were dissolved in 3 mL of chloroform or benzene. To this solution was added 3 mL of acetic acid, and the resulting solution was thermostated for an appropriate period of time at 25 or 50 °C. The precipitated cyclopallated complex was filtered off and washed first with acetic acid and then with hexane.

Study of Equilibrium 2. A solution of $[Pd(dmba)Cl]_2$ (or $[Pd(deba)Cl]_2$) (0.044 mmol) and deba (or dmba) (0.088 mmol) in 3 mL of $CHCl_3$ was mixed with 3 mL of HOAc. The mixture was thermostated at 50 °C for 24 h. The reaction mixture was quenched with 10 mL of $CHCl_3$ diluted with water (25 mL). The aqueous layer was washed with 10 mL of $CHCl_3$, and organic fractions were combined, washed twice with water, and dried over $MgSO_4$. The solution was then concentrated and passed through a silica gel column ($CHCl_3$ eluent), removing free amines. The relative amounts of $[Pd(dmba)Cl]_2$ and $[Pd(deba)Cl]_2$ were determined by ^1H NMR.

Bis(μ-chloro)bis(*N*,*N*-diethyl-4-nitrobenzylaminato-C^2,*N*)dipalladium(II), $[Pd(deba\text{-}NO_2)Cl]_2$. This compound has not been previously reported in the literature. It was prepared by the general procedure described above. Anal. Calcd for $C_{22}H_{30}N_4O_4Cl_2Pd_2$: C, 37.9; H, 4.3; Cl, 10.2. Found: C, 38.4; H, 4.6; Cl, 10.6. Data are as follows: mp 212 °C dec; IR (KBr) 1520 and 1340 cm^{-1} (NO_2); ^1H NMR ($CDCl_3$, in the presence of py-d_5) δ 7.79 (dd, ^3J = 8 Hz, ^4J = 2 Hz, 5 H), 7.03 (d, ^3J = 8 Hz, 6 H), 6.73 (d, ^4J = 2 Hz, 3 H), 4.02 (s, Ar–CH_2–N), 3.41 (m, N–$CH^{\alpha}H^{\beta}$–Me), 2.71 (m, N–$CH^{\alpha}H^{\beta}$–Me), 1.58 (t, CH_2–CH_3).

Acknowledgment. We thank Dr. V. A. Polyakov for recording the ^1H NMR spectra.

Registry No. $[Pd(azb)Cl]_2$, 14873-53-1; $[Pd(deba\text{-}NO_2)Cl]_2$, 88337-15-9; $[Pd(ba)Cl]_2$, 20523-73-3; $[Pd(8\text{-}mq)Cl]_2$, 28377-73-3; $[Pd(dmba)Cl]_2$, 18987-59-2; $[Pd(deba)Cl]_2$, 33571-42-5; $[Pd(damf)Cl]_2$, 58616-62-9.

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