Since $e_1 >> e_2$, $i\varepsilon \approx e_i i$ for low values of $i\varepsilon$. Functions ω_i in Eq. (6) have maxima at $i = N/B$ [1]. Thus, for small N/B, this approximation will be valid. Substituting $\varepsilon_i = e_i i$ into Eq. (6), we obtain $(\partial E/\partial N)_T = e_1$. Therefore, in this approximation, $(\partial E/\partial N)$ will be independent of temperature. According to Eqs. (7) and (9), this indicates the approximate invariance of the slope of the adsorption isosteres at low occupancies.

CONCLUSIONS

1. The description of the isotherms for argon adsorption on zeolite NaX in broad pressure and temperature ranges proposed by Ruthven and others was shown to be unsatisfactory.

2. A new expression for the partition function of i species in a zeolite cavity was obtained which significantly improves the description of the experimental data.

3. The isosteric heats calculated using the parameters found qualitatively agree with the literature data.

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CYCLOPALLADATION OF N-PHENYLBENZAMIDINE

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547.821

Pd^{2+} complexes which are products of cyclopalladation reactions may be used in organic synthesis, in particular, for the preparation of nitrogen heterocycles [1]. For these purposes, it is apparently most convenient to use palladium rings (PR) in which the palladium atom is bound to an NH or NH_2 group [2]. However, such compounds are more available than the corresponding PR containing a fully substituted nitrogen atom. For example, the cyclopalladation of secondary benzylamines is possible only when these amines contain substituents in the α-position [3, 4]. Unsubstituted benzylamine (BA) reacts with PdX_2 salts to give bis-adducts $PdX_2(BA)_2$ [5], of which conversion to a PR upon the action of $AgBF_4$ has been described only for the complex with X = I [6].

We selected N-phenyl-benzylamidine (PBA) as the starting nitrogen base for the synthesis of a cyclic system with a PdNH fragment. The cyclopalladation of N,N-diarylacetamidines gives six-membered PR although the yields and physical indices of these products were not given [7]. However, an alternative pathway is possible for the reaction of PBA with Pd^{2+} salts involving palladation of the Ph—C group of the amidine and formation of a five-membered PR. Structures with five-membered rings have been considered more favorable for PR than six-membered rings

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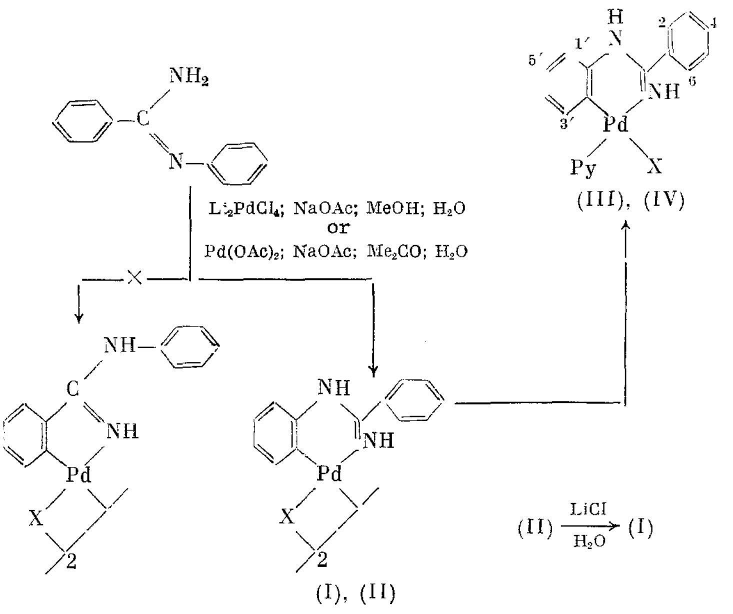
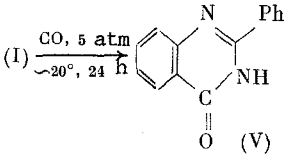
[5, 8]. In contrast, the reaction of PBA with Li_2PdCl_4 or $Pd(OAc)_2$ in the presence of NaOAc gave complexes (I) and (II) with a CPdNH fragment in the six-membered ring in 97 and 81% yield, respectively.



X = Cl (I), (III); X = OAc (II), (IV).

Complex (II) is smoothly converted to (I) by the action of LiCl. The treatment of (I) and (II) with pyridine gave monomeric complexes (III) and (IV). Carbonylation of (I) under mild conditions gave 2-phenyl-4(3H)-quinazolinone (V) in 85% yield.



This conversion confirms the structure of cyclopalladation products (I) and (II). The direction of the electrophilic attack of Pd^{2+} in the case of PBA is apparently largely a function of electronic factors rather than steric factors. The effect of the imidine system likely leads to enhanced electron density at the ortho-carbon atoms of the aromatic ring bound to the nitrogen atom (relative to the corresponding atoms of the Ph–C group, we should expect an opposite effect), which favors the formation of six-membered PR.

The signal for the $H^{3'}$ proton in the PMR spectra of (III) and (IV) is found at higher field (6.3-6.4 ppm) than the signals for the other aromatic protons [9]. The IR spectrum of (II) has strong bands for the bridging acetate groups at 1568 and 1422 cm^{-1} lacking in (IV). We may assume that the facile synthesis of quinazolinone (V) does not exhaust the possibilities of the use of PR (I) and (II) for the preparation of nitrogen heterocycles.

EXPERIMENTAL

The cyclopalladation was carried out in an argon atmosphere. The PMR spectra were carried out on a Bruker WM-250 spectrometer. The IR spectra were taken on a UR-20 and Specord-80M spectrometers in vaseline mulls and KBr pellets. The mass spectra were taken on a Varian MACH-6 spectrometer. The UV spectra were taken on a Specord UV-VIS spectrometer.

Di-μ-chlorobis(2-N-benzimidoylaminophenyl-C,N^2-palladium) (I). A mixture of 708 mg $PdCl_2$ and 379 mg LiCl in 10 ml methanol was stirred for 40 min at 20°C. Then, 332 mg NaOAc and 2 ml water were added and the mixture was stirred for 10 min. A sample of 782 mg PBA was added and 15 ml methanol was added and the mixture was heated at reflux for 15 min. A yellow precipitate formed and the mixture was evaporated to dryness. The precipitate was washed on the filter with water until chloride ions were no longer detected and dried at 60°C (1 mm) to give 1.305 g (97%) (I), mp 235-240°C (dec.). Found: C 46.39; H 3.58; Cl 10.57; N 8.52; Pd 31.89%. Calculated for $C_{13}H_{11}ClN_2Pd$: C 46.32; H 3.29; Cl 10.52; N 8.31; Pd, 31.56%. IR spectrum (ν, cm^{-1}): 3382, 3364 (NH), 1624 (C=N), 232 (Pd–Cl). UV spectrum (DMSO): λ_{max} 300 nm (ε 5100 liters/mole·cm). Mass spectrum, m/z: 194 $[1/2M-HPdCl]^+$.

Di-μ-acetatobis(2-N-benzimidoylaminophenyl-C,N^2-palladium) (II). A mixture of 263 mg PBA, 230 mg $Pd(OAc)_2$, and 97 mg NaOAc in 12 ml aqueous acetone (5:1) was heated at reflux for 20 min. The organic layer was separated and cooled. The yellow precipitate formed was filtered off, washed with two 1-ml portions of acetone, and dried at 70°C (1 mm) to give 343.5 mg (81%) (II), mp 185-188°C (dec.). Found: C 49.39; H 3.98; Pd 28.85%. Calculated for $C_{15}H_{24}O_2N_2Pd$: C 49.95; H 3.91; Pd 29.50%. IR spectrum (ν, cm^{-1}): 3360 br (NH), 1636 (C=N), 1568, 1422 (bridging OAc). UV spectrum (DMSO): λ_{max} 300 nm (ε 4700 liters/mole·cm). Mass spectrum, m/z: 194 $[(1/2)M-HPdOAc]^+$.

Conversion of complex (II) to complex (I). A sample of 1.4 mg LiCl in 10 ml water was added to 133 mg (IV) in 40 ml acetone and stirred for 6 h. The organic layer was separated. The solvent was evaporated in vacuum. The residue was dissolved in CH_2Cl_2, washed with water, and dried over Na_2SO_4 to give 116.5 (94%) (I).

Pyridinechloro(2-N-benzimidoylaminophenyl-C,N^2)palladium (III). A sample of 59 mg pyridine was added to a suspension of 120 mg (I) in 5 ml CH_2Cl_2 and stirred for 1 h at 20°C. The solvent was distilled off. The solid residue was dissolved in acetone and reprecipitated by the addition to hexane to give 120 mg (81%) complex (III) as colorless prisms, mp 163-168°C (dec.). Found: C 51.87; H 3.98; Cl 8.45; Pd 25.37%. Calculated for $C_{18}H_{15}ClN_3Pd$: C 52.07; H 3.64; Cl 8.54; Pd 25.63%. IR spectrum (ν, cm^{-1}): 3376, 3368 (NH), 1620 s (C=N). UV spectrum (EtOH): λ_{max} 292 nm (ε 5900 liters/mole·cm). PMR spectrum in acetone-d_6 (δ, ppm, J, Hz): 6.40 d. d (1H, $H^{3'}$, $J_{H^{3'}4'}$ = 7.5, $J_{H^{3'}5'}$ = 1.5), 6.62 t. d (1H, $H^{4'}$, $J_{H^{4'}5'}$ = 7.5, $J_{H^{4'}6'}$ = 1.5), 7.0 t. d (1H, $H^{5'}$), 7.19 d. d (1H, $H^{6'}$), 7.50-7.66 m (5H, $2H_\beta$, Py, H^3, H^4, H^5), 7.78 m (2H, H^2, H^6), 8.03 t. t (1H, H_γ, Py, $J_{H_\gamma H_\beta}$ = 7.5, $J_{H_\gamma H_\alpha}$ = 1.7), 8.89 m (2H, H_α, Py), 9.60 br. s and 6.88 br. s (2H, NH).

Pyridinacetato-(2-N-benzimidoylaminophenyl-C,N^2)palladium (IV). Complex (IV) was obtained by analogy to complex (III). The yield after recrystallization from 2:5 acetone-hexane was 97%, mp 148-155°C (dec.). Found: C 54.84; H 4.45; Pd 24.83%. Calculated for $C_{20}H_{19}N_3O_2Pd$: C 54.62; H 4.35; Pd 24.19%. IR spectrum (ν, cm^{-1}): 1632 (C=N). UV spectrum (EtOH): λ_{max} 290 nm (ε 6950 liters/mole·cm). PMR spectrum in $CDCl_3$ (δ, ppm): 1.92 br. s (3H, AcO), 6.32 d (1H, $H^{3'}$), 6.65 m (1H), 7.02-7.58 m (9H, arom. and H_β, Py), 7.79 t (1H, H_γ, Py), 8.51 d (2H, H_α, Py), 8.88 br. s and 8.95 br. s (2H, NH). Mass spectrum, m/z: 194 $[M-Py-PdHOAc]^+$.

2-Phenyl-(3H)-quinazolin-4-one (V). A suspension of 187 mg (I) in 15 ml abs. methanol was maintained in an autoclave under 5 atm CO pressure at 20°C for 24 h. The black palladium precipitate was filtered off through Celite and washed with water, five 20-ml portions of ethanol, and 10 ml methanol. The filtrate was evaporated and then 5 ml conc. aq. NH_3 was added. The solution was saturated with NaCl and extracted with three 10-ml THF portions. The extract was dried over Na_2SO_4. The solvent was dissolved off and the residue was dried at 1 mm Hg to give 121 mg (97%) (V). Recrystallization from ethanol gave 105 mg (85%) (V) identical to a sample obtained according to Hagiwara et al. [10], mp 242-243°C. Mass spectrum, m/z: 222 (M^+), 119, 104.

CONCLUSIONS

1. The palladation of N-phenylbenzamidine by Pd^{2+} salts proceeds at the Ph-N group with the formation of a six-membered palladium ring (PR) and not at the Ph-C group with the formation of a five-membered ring.

2. The carbonylation of the PR of (I) under mild conditions gave 2-phenyl-(3H)-quinazolin-4-one.

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