Halogenation of Palladium(II) Complexes of β-Ketoamines

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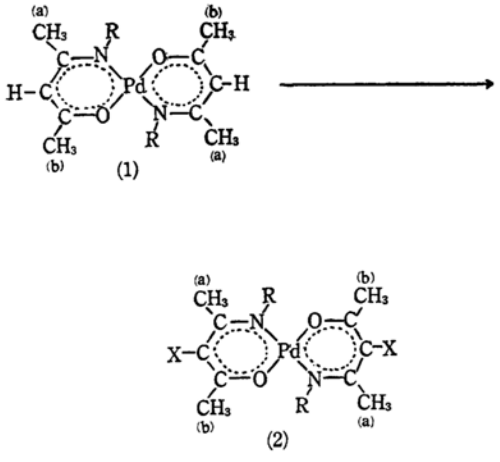
Recenty, Collman has described electrophilic substitution reactions of chromium (III), cobalt (III), and rhodium (III) acetylacetonates[1]; furthermore, we have reported that divalent palladium acetylacetonate has a pseudo-aromatic nature and undergoes an electrophilic substitution at the central carbon of the chelate ring.[2] An investigation of the chemistry of the inert metal chelates of β-ketoamine, the mononitrogen analogs of acetylacetonates, seems a logical sequel to these earlier studies; along these lines, Collman and Kittleman[3] have reported on the bromination of the chromium (III) complexes of β-ketoamines. In the present work, the palladium(II) complexes (1) of β-ketoamines derived from aromatic amines (aniline, *p*-toluidine, and α-naphthylamine) and acetylacetone were found to undergo facile halogenation with *N*-halosuccinimides at the central carbon atom of the chelate ring in the manner of a quasi-aromatic system (*cf.* Fig. 1).



(1)

(2)

Fig. 1

Experimental[4]

Materials. Bis(4-anilino-3-penten-2-one)palladium(II) (1, R=phenyl) and bis(4-*p*-toluidino-3-penten-2-one)palladium(II) (1, R=*p*-tolyl) were prepared by the procedure of Yamada.[5] Bis(4-α-naphthylamino-3-penten-2-one)palladium(II) (1, R=α-naphthyl) was prepared from potassium tetrachloropalladate and α-naphthylamino-3-penten-2-one according to Yamada's method[5] (dec. p. 220—223°C).

General Procedure for Preparing the Halogenated Palladium(II) Complex. Bis(3-chloro-4-anilino-3-penten-2-one)palladium(II). A solution of 0.454 g (0.001 mol) of bis(4-anilino-3-penten-2-one)palladium(II) and 0.267 g (0.002 mol) of *N*-chloro succinimide in 25 m*l* of chloroform was boiled for 5 min, and then evaporated to dryness. The crude complex was separated from succinimide by ether extraction. After the removal of the ether, the resulting residue was chromatographed

TABLE 1. CHARACTERIZATION OF BIS(3-HALO-β-KETOAMINO)PALLADIUM(II) COMPLEXES (2)

R	X	Mp, °C	C%		H%		N%	
			Calcd	Found	Calcd	Found	Calcd	Found
Phenyl	Cl	214—215	50.45	50.64	4.23	4.18	5.34	5.45
Phenyl	Br	191—194*	43.13	43.31	3.61	3.78	4.57	4.49
p-Tolyl	Cl	216—217**	52.22	52.37	4.74	4.71	5.07	5.11
p-Tolyl	Br	185—187**	44.96	44.86	4.09	4.15	4.37	4.44
α-Naphthyl	Cl	205—207*	57.75	57.80	4.20	4.09	4.99	4.87
α-Naphthyl	Br	180—182**	50.55	50.66	3.67	3.55	3.93	3.91

* Decomposed point. ** Melted with decomposition.

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[1] a) J. P. Collman, "Reactions of Coordinated Ligands and Homogeneous Catalysis," ed. by R. F. Gould, Advances in Chemistry Series, No. 37, American Chemical Society, Washigton, D. C. (1963), p. 78. b) J. P. Collman, *Angew. Chem.*, **77**, 154 (1965). c) J. P. Collman, "Transition Metal Chemistry," Vol. II, ed. by R. L. Carlin, Marcel Dekker, New York (1966), p. 1.

[2] A. Kasahara, K. Ujiie and K. Tanaka, This Bulletin, **39**, 2227 (1966).

[3] J. P. Collman and E. T. Kittleman, *Inorg. Chem.*, **1**, 499 (1962).

[4] All melting points are uncorrected. The infrared spectra were measured on KBr disks with a Hitachi EPI-S infrared spectrometer, while the ultraviolet absorption spectra were measured with a Hitachi recording spectrophotometer, model EPS-3T. The NMR spectra were recorded by a Hitachi H-60 instrument.

[5] E. Yoshida and S. Yamada, This Bulletin, **38**, 2179 (1965).

TABLE 2. ULTRAVIOLET SPECTRA* AND NUCLEAR MAGNETIC SPECTRA** (AT 60 Mc/sec) OF PALLADIUM COMPLEXES OF β-KETOAMINES (2)

Compound		λ_{max}, mμ (log ε)	Chemical shifts of protons				
R	X		CH_3(a)	CH_3(b)	X	H of aromatic rings	CH_3 on aromatic rings
Phenyl	H	344(3.93)	8.66(3)	8.37(3)	5.18(1)	3.14—2.55(5)	
Phenyl	Cl	362(4.01)	8.38(3)	8.13(3)	—	3.22—2.65(5)	
Phenyl	Br	361(4.07)	8.31(3)	8.05(3)	—	3.20—2.60(5)	
p-Tolyl	H	345(3.90)	8.61(3)	8.34(3)	5.19(1)	3.28—2.85(4)	7.70(3)
p-Tolyl	Cl	360(3.96)	8.36(3)	8.12(3)	—	3.25—2.84(4)	7.69(3)
p-Tolyl	Br	361(3.98)	8.28(3)	8.00(3)	—	3.23—2.80(4)	7.68(3)
α-Naphthyl	H	345(3.95)	8.64(3)	8.35(3)	5.20(1)	3.25—2.60(7)	
α-Naphthyl	Cl	360(4.02)	8.35(3)	8.11(3)	—	3.24—2.54(7)	
α-Naphthyl	Br	361(4.03)	8.30(3)	8.07(3)	—	3.25—2.55(7)	

* Chloroform was used as solvent.

** NMR data are expressed as τ value and deuterochloroform was used as solvent, using tetramethylsilane as an internal reference. Relative peak intensities in parentheses.

on alumina using dichlorometane. Recrystallization from benzene afforded 0.254 g (45% yield) of yellow crystals, mp 214—215°C (dec.). IR Spectrum (KBr): 1560, 1434, and 1380 cm^{-1}.

Table 1 summarizes the halogenated complexes that have been synthesized by this method. The yields of the purified complexes ranged from 30 to 50%.

Discussion

The infrared spectrum of bis(4-anilino-3-penten-2-one)palladium(II) (1, R=phenyl) exhibits strong and characteristic peaks at 1585 and 1512 cm^{-1}. This characteristic pattern of the infrared maxima is shown by all of the β-ketoamine complexes examined. The replacement of the hydrogen by the halogen at the central carbon atom resulted in the disappearance of the bands at 1585 and 1512 cm^{-1} and their replacement by a strong peak at 1560 cm^{-1}. This behavior is analogous to that of the spectra of the metal acetylacetonates. Dryden[6] observed that the replacement of the hydrogen by other groups at the central carbon of metal acetylacetonate rings caused the infrared doublet in the 1500—1600 cm^{-1} region to become a singlet at about 1550 cm^{-1}. An example of this empirical rule has also been observed in the series of the chromium(III) complexes of β-ketoamines.[3] Furthermore, bis(4-anilino-3-penten-2-one)palladium (II) (1, R=phenyl) shows a medium band at 1204 cm^{-1}, but there is no absorption peak at 1200 cm^{-1} in the spectra of the halogenated complexes. The medium band at 1199 cm^{-1} in the spectra of palladium acetylacetonate has previously been assigned to the bending mode of the hydrogen at the central carbon atom;[7] the absence of this peak is unequivocal evidence of the replacement at the central carbon of acetylacetonates.[8]

The nuclear magnetic resonance spectra summarized in Table 2 provide conclusive proof of the structure assigned to the halogenated complexes (2). The unhalogenated complex (1, R=phenyl) exhibits proton signals at 8.66, 8.37, 5.18, and 3.14—2.55 τ, with relative intensities of 3 : 3 : 1 : 5. These signals may be assigned to the methyl protons (a), methyl protons (b), the hydrogens on the center carbon, and the aromatic protons (*cf.* Fig. 1). On the other hand, the halogenated complex, bis(3-chloro-4-anilino-3-penten-2-one)palladium(II (2, R=phenyl, X=Cl), gives signals at 8.38, 8.13, and 3.22—2.65 τ, with relative intensities of 3 : 3 : 5. These signals may be assigned to the methyl protons (a), methyl protons (b), and the aromatic protons, respectively. The ultraviolet spectra of the palladium(II) complexes of β-ketoamines are summarized in Table 2. The introduction of the halogen into the chelate rings gives rise to a bathochromic shift in each of the ultraviolet maxima, suggesting an increased conjugated system.

Preliminary attempts to carry out the nitration and acetylation of this complex system were unsuccessful. Under the same conditions that had previously effected the nitration of palladium(II) acetylacetonate,[2] the β-ketoamine complexes were destroyed. The latter showed much less stability under acidic conditions.

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6) R. P. Dryden and A. Winston, *J. Phys. Chem.*, **62**, 635 (1958).

7) K. Nakamoto, P. J. McCarthy and A. E. Martell, *J. Am. Chem. Soc.*, **83**, 1272 (1961).

8) J. P. Collman, R. L. Marshall, W. L. Young, II, and S. D. Goldby, *Inorg. Chem.*, **1**, 704 (1962).