

RING-OPENING REACTION OF PALLADIACYCLOPENTADIENE COMPLEX
WITH N,N-DICHLOROAMINE AND -AMIDE

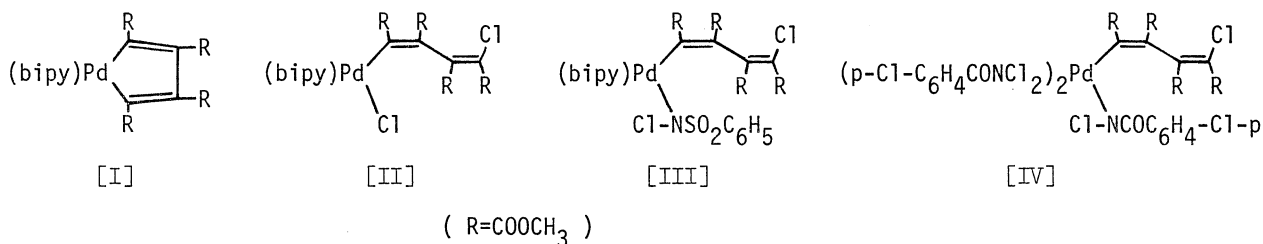
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Reactions of the palladiacyclopentadiene complex, $\text{Pd}(\text{C}_4\text{R}_4)(\text{bipy})$ [$\text{R}=\text{COOCH}_3$], with N,N-dichloroamine and -amide afforded three different σ -4-chloro-1,2,3,4-tetrakis(methoxycarbonyl)buta-1,3-dienyl-palladium complex [II], [III], and [IV]. No nitrene adducts were formed.

Recently the chemical behavior of the N-haloamines has been investigated extensively.¹⁾ N,N-Dichloroamine or -amide is expected to generate nitrene in the reaction with low valent noble metal complexes which would readily tend to form metal dichloride, L_nMCl_2 , oxidatively. Maitlis²⁾ reported that the palladiacyclopentadiene complex afforded the acetylenic trimer. A reaction of this complex with nitrene, generated by a metal-assisted reactions of N,N-dichloroamine or -amides, is expected to give pyrrole in a similar fashion. In order to examine the possibility of a metal-assisted nitrene generation, this letter describes the reaction between palladiacyclopentadiene bipyridine complex [I] with four N,N-dichloroamine and -amides.

An equimolar mixture of palladiacyclopentadiene complex [I] and N,N-dichloro-t-butylamine or N,N-dichloro-p-toluamide in benzene was kept at room temperature. After 10 hr stirring, σ -4-chloro-1,2,3,4-tetrakis(methoxycarbonyl)buta-1,3-dienyl-palladium complex [II] precipitated, which was recrystallized from CH_2Cl_2 as pale yellow crystals. The reaction of [I] with N,N-dichlorobenzenesulfonamide or N,N-dichloro-p-chlorobenzamide under similar reaction conditions gave [III] or [IV], respectively. In both cases, any nitrene adduct with the ligand $\text{C}_4(\text{COOCH}_3)_4$ was not isolated.

Three resonance peaks at τ 6.57(3H), 6.36(6H), and 6.30(3H) due to the methoxycarbonyl group appeared in the ^1H nmr spectrum of [II] in CD_3COCD_3 , whereas the original palladiacyclopentadiene complex [I] showed only one resonance peak at τ 6.25 in CDCl_3 or two peaks at τ 6.34 and 6.32 in CD_2Cl_2 . Similarly [III] and [IV] showed four resonance peaks in the methoxycarbonyl region. This nmr result strongly suggests that [II], [III], and [IV] have the linear (σ -1,3-butadienyl) structures by the cleavage of one Pd-C bond of the five-membered metallocycles.



In ir spectra, [II] had an absorption band of the Pd-Cl stretching vibration at 323 cm⁻¹, while no absorptions appeared around this region in those of [III] and [IV]. In addition, [IV] showed three absorptions at 1737, 1720, and 1689 cm⁻¹ due to carbonyl stretching vibrations. The absorption at 1737 cm⁻¹ could be assigned to the carbonyl stretching frequency of p-Cl-C₆H₄CONCl₂ ligand. The data of mass spectrum of [IV] were also well consistent with the proposed structure.

It is indicated that the delocalization of lone pair electrons by electron-withdrawing carbonyl or sulfonyl groups increased the stability of the Pd-N σ-bond in [III] and [IV]. The formation of [IV] is explained in terms of the Pd-C bond cleavage of [I] by the attack of the N-Cl bond and the subsequent ligand exchange of bipyridine by N,N-dichloro-p-chlorobenzamide. The mp, ir, and nmr data of [II], [III], and [IV] are summarized in following Table. Satisfactory analyses for all new complexes were obtained.

Table. The mp, ir, and nmr data of [II], [III], and [IV].

Complex	Yield (%)	mp (°C)	$\nu_{C=O}$, ν_{Pd-Cl} (cm ⁻¹)	τ_{COOCH_3}
II	64 ^{a)} 73 ^{b)}	168.0-170.0	1722 , 323	6.57 (3H), 6.36 (6H) 6.30 (3H)
III	84	185.0-186.0	1722 —	6.92 (3H), 6.29 (3H) 6.20 (3H), 6.16 (3H)
IV	57	115.5-117.5	1737 — 1720 1689	6.36 (3H), 6.34 (3H) 6.30 (3H), 6.18 (3H)

a), b); N,N-Dichloro-t-butylamine and N,N-dichloro-p-toluamide were used as reagents, respectively.

The detailed and extended analysis of this reaction is now in progress.

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