Journal of Organometallic Chemistry, 280 (1985) C51—C53
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

METALLATION OF ALIPHATIC CARBON ATOMS

II*, SYNTHESES AND CHARACTERIZATION OF THE CYCLOPALLADATED COMPLEXES OF *N,N*-DIMETHYLNEOPENTYLAMINE

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(Received August 18th, 1984)

Summary

N,N-Dimethylneopentylamine reacts with $Pd(MeCO_2)_2$ to give a novel trinuclear cyclopalladated complex $[Me_2NCH_2CMe_2CH_2Pd(\mu\text{-}MeCO_2)_2Pd(\mu\text{-}MeCO_2)_2PdCH_2CMe_2CH_2NMe_2] \cdot 0.5C_6H_6$ (I). The reaction of I with PPh_3 affords both *trans*-$[Pd(MeCO_2)_2(PPh_3)_2]$ (II) and $[Pd(CH_2CMe_2CH_2NMe_2)(MeCO_2)(PPh_3)]$ (III). The reaction of III with LiCl yields a mononuclear cyclopalladated complex, $[Pd(CH_2CMe_2CH_2NMe_2)Cl(PPh_3)]$ (IV).

Metallation of an aliphatic carbon atom has been one of the current topics in organometallic chemistry in association with the activation of C—H bonds by transition metals [1]. Recently, we [2] reported the syntheses of the six-membered cyclopalladated complexes of 2-neopentylpyridine through direct metallation of the aliphatic carbon atom by use of $Pd(MeCO_2)_2$. This communication deals with the cyclopalladation of *N,N*-dimethylneopentylamine by $Pd(MeCO_2)_2$, resulting in the formation of a novel trinuclear cyclopalladated complex.

N,N-Dimethylneopentylamine (5.5 mmol) reacted with $Pd(MeCO_2)_2$ (4.45 mmol) in benzene (20 ml) at 50—55°C for 1.5 h. After the mixture was filtered to remove the precipitated palladium black, the filtrate was concentrated under reduced pressure and diluted with hexane to give a novel trinuclear cyclopalladated complex, $[Me_2NCH_2CMe_2CH_2Pd(\mu\text{-}MeCO_2)_2Pd(\mu\text{-}MeCO_2)_2PdCH_2CMe_2CH_2NMe_2] \cdot 0.5C_6H_6$ * (I) in 36% yield (Scheme 1).

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*Satisfactory elemental analysis and ^1H NMR data were obtained.

0022-328X/85/$03.30

Complex I was not isolated from the reaction mixture either in acetic acid at 70° C or in methanol at 60° C.

When *N*,*N*-dimethylneopentylamine was treated with $Pd(MeCO_2)_2$ in a molar ratio of 2/3 or 1/1 in $CDCl_3$ at 19° C, it was observed by ^1H NMR spectroscopy that I was formed smoothly. As for the reaction in the molar ratio of 2/1, I was produced in lower yield (about 10% after 4 h), and a large amount of palladium black was formed. In no case was any other cyclopalladated complex, such as a binuclear one, detected.

Complex I reacted with PPh_3 to produce *trans*-$[Pd(MeCO_2)_2(PPh_3)_2]$ (II) in 56% yield, as well as an oily product, $Pd(CH_2CMe_2CH_2NMe_2)(MeCO_2)(PPh_3)$* (III). The IR spectrum of II coincided quite well with that of the authentic sample [3]. The oily product III was uncrystallizable and was converted into $Pd(CH_2CMe_2CH_2NMe_2)Cl(PPh_3)$ (IV) in 55% yield (based on I) by reaction with LiCl.

The IR spectrum of I exhibited $\nu(COO^-)$ frequencies due to bridging acetato groups at 1610(s), 1570(s), 1405(s), 1380(s), and 1335(s) cm^{-1}, which were very similar to those of the trimeric palladium(II) acetate [3]. The ^1H NMR spectrum of IV in $CDCl_3$ exhibited two methylene proton signals at δ 1.34 (d, $^3J(HP)$ 4.5 Hz; Pd—CH_2) and 2.50 ppm (s, N—CH_2) and two methyl proton signals at δ 1.02 (s, CMe_2) and 2.89 ppm (d, $^4J(HP)$ 2.5 Hz; NMe_2). The resonance at δ 1.34 ppm was assigned to the protons of the palladium-bonded methylene group which was produced by the cyclopalladation of *N*,*N*-dimethylneopentylamine. The coupling of the protons of both Pd-CH_2 and NMe_2 with the ^{31}P nucleus confirmed strongly the presence of a CH_2 ....NMe_2 chelate structure. The small coupling constant $^3J(HP)$ for Pd-CH_2 suggests that PPh_3 is situated in a *cis* position to the palladated methylene carbon. These facts indicate unambiguously that I contains both the $Pd(CH_2CMe_2CH_2NMe_2)(MeCO_2)$ and $Pd(MeCO_2)_2$ moieties. On the basis of these discussions, the elemental analysis, and the molecular weight (745.1 in benzene, calcd. 783.9), complex I was assigned to have trinuclear structure, which involves four acetato bridges and two $Me_2NCH_2CMe_2CH_2$-C^1,*N* chelates. It is noteworthy that *N*,*N*-dimethylneopentylamine reacted with $Pd(MeCO_2)_2$ in hot benzene to afford directly the trinuclear cyclopalladated complex, I. Ukhin et al. [4] reported that $Pd(MeCO_2)_2$ reacted with 2,6-disubstituted pyrylium salts to afford trinuclear bis(1-3-η-1,3-diacylallyl)tripalladium(II) complexes having four μ-acetato ligands.

As for the ^1H NMR spectrum of I in $CDCl_3$ at 14° C, the acetato-methyl protons appeared as four singlets at δ 1.78 (2.4H), 1.80 (2.4H), 1.82 (3.6H), and 1.84 ppm (3.6H), indicating that I contains both an (*a*-C^1,*b*-*N*)-(*k*-C^1,*l*-*N*)-type (*ak*-type) isomer and an (*a*-C^1,*b*-*N*)-(*k*-*N*, *l*-C^1)-type (*al*-type) isomer (Scheme 1) in a ratio of about 2/3. In addition, I exhibited two sets of signals corresponding to the two isomers. At 14° C, one set consisted of six signals at δ 1.33 (s, H_3CCCH_3), 1.36 (s, H_3CCCH_3), 2.40 (q, $\Delta\delta$ 0.29 ppm, $^2J(HH)$ 8 Hz, Pd—CH_2), 2.45 (q, $\Delta\delta$ 0.29 ppm, $^2J(HH)$ 9 Hz, N—CH_2), 2.88

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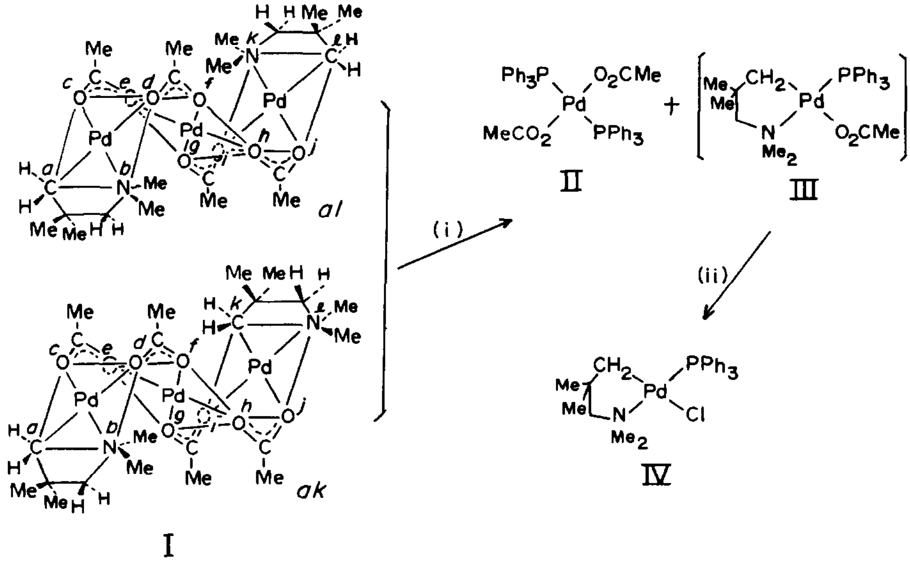
*The ^1H NMR spectrum of III was very similar to that of IV, except for the acetato-methyl proton resonance at δ 1.54 ppm.



SCHEME 1. Reagents: i, PPh_3; ii, LiCl.

(s, H_3CNCH_3), and 3.01 ppm (s, H_3CNCH_3) and was temperature-dependent. At 43°C the two C-methyl proton signals united to give one singlet at δ 1.34 ppm, whereas the two *N*-methyl proton signals coalesced into one singlet at δ 2.98 ppm; then, the two quartets changed into broad signals. The other set involved four singlets at δ 1.27 [$C(CH_3)_2$], 2.73 (Pd—CH_2), 2.93 (N—CH_2), and 3.01 ppm [$N(CH_3)_2$] * and virtually did not change in the range −35—43°C. The temperature-dependency of the ^1H NMR spectra of I was associated with the inversion of the acetato bridges, as observed for the other binuclear acetato-bridged complexes [5,6]. The inversion corresponding to the former set was actually quenched below 20°C, whereas that corresponding to the latter set was not quenched even at −35°C.

The ^{13}C-{^1H} NMR data of I in $CDCl_3$ at 24°C are quite consistent with the presence of the two isomers, showing four carboxylato carbon signals at δ 181.6, 181.9, 183.4, and 183.5 ppm, two acetato-methyl carbon signals at δ 22.4 and 23.4 ppm, and two C-methyl carbon signals at δ 28.3 and 28.6 ppm. In addition, I exhibited four singlets at δ 35.9 (Pd—CH_2), 43.8 (CMe_2), 54.3 [$N(CH_3)_2$], and 80.3 (NCH_2).

The stability of I, III, and IV is associated with both the chelate structure of the $PdCH_2CMe_2CH_2NMe_2$ moiety and the lack of β-hydrogen in the 3-(dimethylamino)-2,2-dimethylpropyl group.

Acknowledgements. The present work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education.

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*The singlet at δ 3.01 ppm was ascribed to protons of one of two *N*-methyl groups of the former set and those of two *N*-methyl groups of the latter set.

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