Synthesis and ligand substitution reactions of a homoleptic acetonitrile dipalladium(I) complex†

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The first homoleptic nitrile dipalladium(I) complex $[Pd_2(CH_3CN)_6][BF_4]_2$ is prepared; the CH₃CN ligand un**dergoes facile displacement by phosphine or bidentate nitrogen ligands while the Pd–Pd bond remains intact.**

Homoleptic transition metal complexes containing weakly coordinated ligands have long been recognized as versatile sources of active catalysts or inorganic functional materials.¹ For example, the combination of an electrophilic $Pd(n)$ complex $[Pd(CH_3CN)_4][BF_4]_2$ 1² and appropriate auxiliary ligands has been frequently used as a pre-catalyst for olefin oligomerization, aromatic substitution, Wacker type oxidation, or alkyne hydroamination reaction.³ While the corresponding homoleptic di- or multi-nuclear complexes of weakly coordinated ligands are relatively rare, several acetonitrile complexes of $Mo\equiv Mo⁴$ Tc=Tc,⁵ Re= Re ,⁶ and Rh–Rh⁷ have been prepared. Here, we report the first synthesis and reactivity of homoleptic acetonitrile dipalladium complex $[Pd_2(CH_3CN)_6][BF_4]_2 \hat{2}$.

When 1 was treated with 0.5 equiv. of $Pd_2(dba)$ ₃ at room temperature in dry $CH_3CN-CH_2Cl_2$, the solution turned reddish-orange. Pouring this solution into $Et₂O$ afforded an orange powder of **2** in 90% isolated yield [eqn. (1)].‡ Elemental

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L = \begin{bmatrix} 2+ & 1/2 \\ -Pd-L & + 1/2 Pd_2(dba)_{3} \\ 1 & 2BF_4 \end{bmatrix} \xrightarrow[H_3CN/CH_2Cl_2]{\begin{bmatrix} 1 & 1/2+ \\ -Pd & -Pd-L \\ 1 & 2 BF_4 \end{bmatrix}} (1)
$$

analysis supported the composition of **2**. UV–VIS spectra of **2** showed a $\sigma-\sigma^*$ transition at $\lambda_{\text{max}} = 436$ nm ($\varepsilon = 1095$ M⁻¹ cm^{-1}). The homoleptic complex 2 was soluble in CD₃CN or $CD₃OD$. In $CD₃OD$, the coordinated acetonitrile protons appeared at δ 2.55, although gradual decomposition occurred with the formation of Pd black. When 2 was dissolved in H_2O , decomposition occurred within 10 min although it has been known that rather stable mononuclear aqua complexes are formed from 1 in H_2O^{3h} It should be mentioned that further addition of 0.5 equiv. of $Pd_2(dba)$ ₃ to 2 in $CH_3CN-CH_2Cl_2$ at room temperature resulted in decomposition instead of the desired formation of Pd_3 complexes such $[Pd_3(CH_3CN)_8]^{2+.8}$

The dipalladium complex **2** underwent facile ligand-substitution reaction with the Pd–Pd bond remaining *intact* under moderate conditions. For example, addition of 2 equiv. of PPh₃ to 2 in CD₃CN afforded bisphosphine dipalladium complex $[Pd_2(CH_3CN)_4(PPh_3)_2][BF_4]_2$ ³⁹ quantitatively [eqn. (2)]. The reaction of 2 with >2 equiv. of PPh₃ afforded several

(2)

unidentified species. On the other hand, controlled addition of an equimolar amount of PPh_3 to a CH_2Cl_2 solution of 2 afforded monophosphine complex $[Pd_2(CH_3CN)_5(PPh_3)][BF_4]_2$ 4 which was detectable by ³¹P NMR spectroscopy (δ 19.3). The position of PPh3 ligand in **4** is suggested to be *cis* to the Pd–Pd bond by considering the relative *trans*-influence of PPh₃, CH₃CN and [Pd] ligands.⁹ Further addition of PPh₃ (1 equiv.) afforded 3 quantitatively. The reaction of **2** with 2 equiv. of bidentate phosphine, dppm (diphenylphosphinomethane), in CD_3CN afforded a known complex $[Pd_2(dppm)_2(CH_3CN)_2][BF_4]_2$ 5¹⁰ quantitatively [eqn. (3)]. The reaction of **2** with 2 equiv. of

1,10-phenanthroline (phen) afforded $[Pd_2(phen)_2(CH_3-]$ CN ₂][BF₄]₂ **6** [eqn. (4)].¹¹ ¹H NMR signals including non-

equivalent H^5 and $H^{5'}$ resonances showing H^5 – $H^{5'}$ coupling (*J* 8.64 Hz). The coordination of $CH₃CN$ in solution was confirmed by observation of a methyl resonance at δ 2.56. The reaction of **2** with *N*,*N*-ethylenebis(benzaldiimine) (diimine) afforded $[Pd_2$ (diimine)₂(CH₃CN)₂][BF₄]₂ **7** [eqn. (5)].

The observation of only one aldimine proton and carbon resonances suggests that the diimine ligands bridge over the Pd– Pd bond unlike phen in **6**. The ethylene proton resonances appearing as an AA'BB' pattern suggest a chiral structure of 7 in solution arising from the non-planar Pd_2N_4 group.

Finally, to test the utility of the homoleptic acetonitrile dipalladium complex **2** as a 'naked' [Pd–Pd]2+ building block of palladium clusters, we examined the preparation of palladium sandwich chains. Thus, the Pd₄ complex $[Pd_4(\mu-\eta^3;\eta^2;\eta^2+\eta^3-$ 1,8-diphenylocta-1,3,5,7-tetraene)2][BF4]2 **8**¹² was prepared

[†] Electronic supplementary information (ESI) available: NMR spectroscopic data and elemental analysis for **6** and **7**. See http://www.rsc.org/ suppdata/cc/b0/b004726k/

(76% after recrystallization) [eqn. (6)] without formation of any

palladium black which was formed in considerable amounts in the previous method from 1, 1.5 equiv. of $Pd_2(dba)_3$ and tetraene.

In summary, we have prepared the first homoleptic nitrile dipalladium(I) complex 2. The nitrile ligands in 2 were proven to be substitutionally labile with the Pd–Pd bond remaining intact. Applications of **2** to catalysis as well as being a potential versatile building block towards palladium clusters are now under investigation.

Notes and references

 \ddagger To a solution of [Pd(CH₃CN)₄][BF₄]₂ (1.00 g, 2.25 mmol) in CH₃CN (50 mL) was added Pd₂(dba)₃**·**CHCl₃ (1.17 g, 1.13 mmol) and CH₂Cl₂ (50 mL). The mixture was stirred for 1 h at room temperature. The reaction mixture was filtered and poured into dry $Et₂O$ to give an orange precipitate. After washing with Et₂O several times, 2 was obtained in 90% yield (1.28 g, 2.02) mmol). IR (Nujol): $v_{C\equiv N}$ 2331, 2307, 2282 cm⁻¹. Anal. Calc. (Found) for Pd₂C₁₂H₁₈N₆B₂F₈: C, 22.78 (22.65); H, 2.87 (2.92); N, 13.28 (13.03%).

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