Synthesis and ligand substitution reactions of a homoleptic acetonitrile dipalladium(1) complex[†]

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The first homoleptic nitrile dipalladium(1) complex $[Pd_2(CH_3CN)_6][BF_4]_2$ is prepared; the CH_3CN ligand undergoes 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. For example, the combination of an electrophilic $Pd(\pi)$ complex $[Pd(CH_3CN)_4][BF_4]_2$ 1^2 and appropriate auxiliary ligands has been frequently used as a pre-catalyst for olefin oligomerization, aromatic substitution, Wacker type oxidation, or alkyne hydroamination reaction. While the corresponding homoleptic di- or multi-nuclear complexes of weakly coordinated ligands are relatively rare, several acetonitrile complexes of $Mo \equiv Mo, Tc \equiv Tc, S$ $Re \equiv Re, G$ and $Rh-Rh^7$ have been prepared. Here, we report the first synthesis and reactivity of homoleptic acetonitrile dipalladium complex $[Pd_2(CH_3CN)_6][BF_4]_2$ 2.

When 1 was treated with 0.5 equiv. of Pd₂(dba)₃ at room temperature in dry CH₃CN-CH₂Cl₂, the solution turned reddish-orange. Pouring this solution into Et₂O afforded an orange powder of 2 in 90% isolated yield [eqn. (1)].‡ Elemental

analysis supported the composition of 2. UV-VIS spectra of 2 showed a σ - σ^* transition at $\lambda_{max} = 436$ 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 H₂O, 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 Pd2(dba)3 to 2 in CH3CN-CH2Cl2 at room temperature resulted in decomposition instead of the desired formation of Pd_3 complexes [Pd₃(CH₃CN)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 $[Pd_2(CH_3CN)_4(PPh_3)_2][BF_4]_2$ **3** 9 quantitatively [eqn. (2)]. The reaction of **2** with >2 equiv. of PPh₃ afforded several

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unidentified species. On the other hand, controlled addition of an equimolar amount of PPh₃ to a CH₂Cl₂ solution of **2** afforded monophosphine complex [Pd₂(CH₃CN)₅(PPh₃)][BF₄]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 CD₃CN afforded a known complex [Pd₂(dppm)₂(CH₃CN)₂][BF₄]₂ **5**¹⁰ quantitatively [eqn. (3)]. The reaction of **2** with 2 equiv. of

1,10-phenanthroline (phen) afforded [Pd₂(phen)₂(CH₃-CN)₂][BF₄]₂ $\bf 6$ [eqn. (4)]. ¹¹ H NMR signals including non-

2 + 2 phen
$$CD_2Cl_2$$
 N Pd Pd N $2BF_4$ (4)

equivalent H⁵ and H⁵′ resonances showing H⁵–H⁵′ 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 [Pd₂(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 $\bf 6$. The ethylene proton resonances appearing as an AA'BB' pattern suggest a chiral structure of $\bf 7$ in solution arising from the non-planar Pd₂N₄ 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 [Pd₄(μ - η ³: η ²: η ²: η 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

- ‡ 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%).
- 1 Synthetic Coordination Chemistry: Principles and Practice, ed. J. A. Davies, C. M. Hockensmith, V. Y. Kukushkin and Y. N. Kukushkin, World Scientific Publishing, 1996, Ch. 4; for recent examples, W. E. Buschmann and J. S. Miller, Chem. Eur. J., 1998, 4, 1731.

- B. B. Wayland and R. F. Schramm, *Inorg. Chem.*, 1965, 4, 427; R. F. Schramm and B. B. Wayland, *Chem. Commun.*, 1968, 898; R. R. Thomas and A. Sen, *Inorg. Synth.*, 1990, 28, 63.
- 3 For selected examples: (a) B. M. Trost, S. A. Godleski and J. P. Genêt, J. Am. Chem. Soc., 1978, 78, 3930; (b) A. Sen and T.-W. Lai, J. Am. Chem. Soc., 1981, 103, 4627; (c) B. M. Trost and J. M. D. Fortunak, Organometallics, 1982, 1, 7; (d) A. Sen and T.-W. Lai, Organometallics, 1982, 1, 415. (e) T.-W. Lai and A. Sen, Organometallics, 1984, 3, 866; (f) L. S. Hegedus, T. A. Mulhern and H. Asada, J. Am. Chem. Soc., 1986, 108, 6224; (g) A. Sen, Acc. Chem. Res., 1988, 21, 421; (h) A. Sen, T.-W. Lai and R. R. Thomas, J. Organomet. Chem., 1988, 358, 567; (i) Z. Jiang and A. Sen, J. Am. Chem. Soc., 1990, 112, 9655; (j) Z. Jiang and A. Sen, Organometallics, 1993, 12, 1406; (k) S. Oi, K. Kashiwagi and Y. Inoue, Tetrahedron Lett., 1998, 39, 6253; (l) Y. Uozumi, K. Kato and T. Hayashi, J. Org. Chem., 1998, 63, 5071.
- 4 F. A. Cotton and K. J. Wiesinger, *Inorg. Chem.*, 1991, **30**, 871; F. A. Cotton, J. L. Eglin and K. J. Wiesinger, *Inorg. Chim. Acta.*, 1992, **195**, 11
- 5 J. C. Bryan, F. A. Cotton, L. M. Daniels, S. C. Haefner and A. P. Sattelberger, *Inorg. Chem.*, 1995, 34, 1875.
- S. N. Bernstein and K. R. Dunbar, *Angew. Chem.*, *Int. Ed. Engl.*, 1992, 31, 1360.
- 7 K. R. Dunbar, *J. Am. Chem. Soc.*, 1988, **110**, 8247; K. R. Dunbar and L. E. Pence, *Inorg. Synth.*, 1992, **29**, 182; M. E. Prater, L. E. Pence, R. Clérac, G. M. Finniss, C. Campana, P. Auban-Senzier, D. Jérome, E. Canadell and K. R. Dunbar, *J. Am. Chem. Soc.*, 1999, **121**, 8005.
- 8 Homoleptic isocyanide di- and tri-palladium complex has been previously synthesized; D. J. Doonan, A. L. Balch, S. Z. Goldberg, R. Eisenberg and J. S. Miller, *J. Am. Chem. Soc.*, 1975, **97**, 1961; J. R. Boehm, D. J. Doonan and A. L. Balch, *J. Am. Chem. Soc.*, 1976, **98**, 4845; A. L. Balch, J. R. Borhm, H. Hope and M. M. Olmstead, *J. Am. Chem. Soc.*, 1976, **98**, 7431.
- 9 T. Murahashi, T. Otani, E. Mochizuki, Y. Kai, H. Kurosawa and S. Sakaki, J. Am. Chem. Soc., 1998, 120, 4563.
- 10 A. Miedaner and D. L. Du Bois, Inorg. Chem., 1988, 27, 2479.
- 11 The analogous isocyanide dipalladium complexes containing bidentate nitrogen ligands have been prepared: T. Tanase, H. Ukaji and Y. Yamamoto, J. Chem. Soc., Dalton Trans., 1996, 3059.
- 12 T. Murahashi, E. Mochizuki, Y. Kai and H. Kurosawa, J. Am. Chem. Soc., 1999, 121, 10660.