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Preliminary communication

Synthesis and characterization of binuclear palladium complexes of isocyanides with novel bridging η^3-indenyl ligands. Crystal structure of $[Pd_2(\mu\text{-}\eta^3\text{-indenyl})_2(RNC)_2]$ (R = 2,6-dimethylphenyl)

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Abstract

The reaction of $PdCl_2(RNC)_2$ (RNC = isocyanide) with indenyl lithium (InLi) gave a binuclear palladium complex, $[Pd_2(\mu\text{-}\eta^3\text{-In})_2(RNC)_2]$, in which the $Pd_2(RNC)_2$ unit is sandwiched between two $\mu\text{-}\eta^3$-indenyl groups in a *syn* arrangement.

The η^5-indenyl (In) transition metal complexes are more reactive in associative and photochemical reactions than their cyclopentadienyl (Cp) analogues, because the reversible slippage of the metal across the five-membered ring can form a reactive η^3-indenyl tautomer that has both benzenoid resonance stabilization and an accessible co-ordination site, the so-called "indenyl ligand effect" [1,2]. In this regard, η^3-indenyl complexes postulated as intermediates have attracted much attention, but structural studies of such complexes are still rare and limited to the monomeric species [3–5]. Werner et al. have reported the binuclear palladium complex $Pd_2(\mu\text{-}\eta^3\text{-Cp})_2(PEt_3)_2$ (**1**), in which two η^3-Cp ligands are co-ordinated sandwich-like to the linear $Pd_2(PEt_3)_2$ unit in an *anti* arrangement [6]. In contrast with Cp complexes, dimeric η^3-indenyl analogues have not been prepared yet. Here, we wish to report a synthesis and characterization of binuclear palladium complexes of isocyanide with novel bridging η^3-indenyl ligands.

A slurry of $PdCl_2(RNC)_2$ (**2**) in benzene was treated with excess indenyl lithium (InLi) for 1 h at room temperature. The resultant dark red solution was chromatographed on deactivated alumina to afford yellow crystals formulated as $Pd_2(In)_2(RNC)_2$ (**3a**: R = 2,6-dimethylphenyl (Xyl), 62%; **3b**: R = 2,4,6-trimethylphenyl (Mes), 51%) [7*]. Compound **3a** was also prepared in a low yield

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* Reference number with asterisk indicates a note in the list of references.

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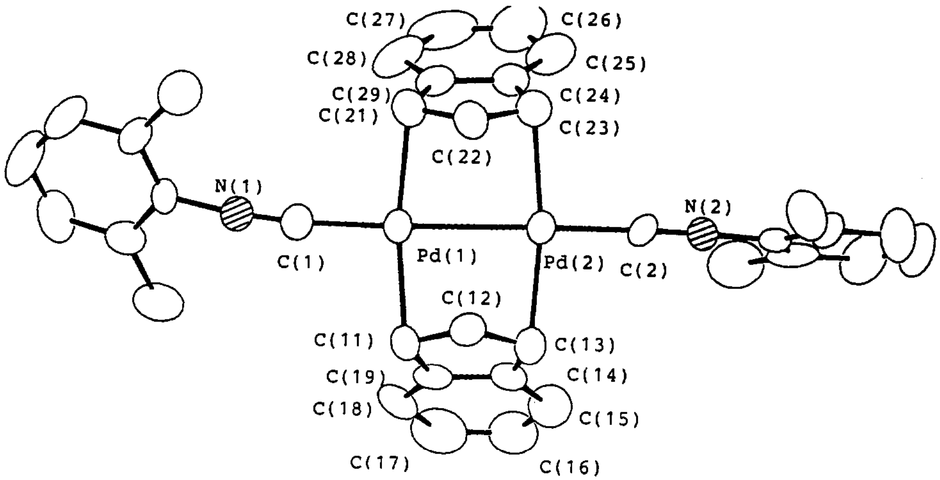

Fig. 1. ORTEP drawing of $[Pd_2(\mu\text{-}\eta^3\text{-In})_2(XylNC)_2]$ (**3a**). Some selected bond distances (Å) and angles (°): Pd(1)–Pd(2) 2.656(2), Pd(1)–C(1) 1.958(14), Pd(1)–C(11) 2.158(14), Pd(1)–C(21) 2.170(15), Pd(1)–C(12) 2.515(13), Pd(1)–C(22) 2.534(15), Pd(2)–C(2) 1.949(13), Pd(2)–C(13) 2.188(15), Pd(2)–C(23) 2.183(15), Pd(2)–C(12) 2.495(13), Pd(2)–C(22) 2.489(14), C(11)–C(12) 1.42(2), C(11)–C(19) 1.52(2), C(12)–C(13) 1.39(2), C(13)–C(14) 1.46(2), C(14)–C(19) 1.41(2), C(21)–C(22) 1.42(2), C(21)–C(29) 1.47(2), C(22)–C(23) 1.39(2), C(23)–C(24) 1.47(2), C(24)–C(29) 1.40(2); Pd(2)–Pd(1)–C(1) 165.8(4), Pd(2)–Pd(1)–C(11) 85.7(4), Pd(2)–Pd(1)–C(21) 85.0(4), Pd(1)–Pd(2)–C(2) 161.6(4), Pd(1)–Pd(2)–C(13) 85.5(4), Pd(1)–Pd(2)–C(23) 86.0(4), Pd(1)–C(1)–N(1) 174.0(12), Pd(2)–C(2)–N(2) 178.2(12).

(15%) by the reaction of the dimeric $Pd_2Cl_2(XylNC)_4$ complex with InLi. The UV-Vis spectra of **3** showed an absorption at 418 nm, assignable to the σ–σ * transition for a metal–metal bond as in other palladium(I) dimers [8]. The IR spectra showed peaks around 2100 cm^{-1} corresponding to the terminal isocyanides. In the ^1H NMR spectra of **3**, characteristic resonances for isocyanide and indenyl ligands were observed at δ ~ 2.3–2.7 (CH_3 of RNC), δ ~ 4.4 (H2 of In), and δ ~ 6.3 (H1 and H3 of In) **, suggesting the presence of one kind of isocyanide and indenyl group. In order to clarify the co-ordination mode of indenyl groups, an X-ray crystallographic analysis of **3a** was undertaken [9*].

The molecular structure of **3a** is shown in Fig. 1. The complex consists of two palladium atoms bridged by two indenyl groups in a *syn* arrangement. The palladium–palladium bond length of 2.656(2) Å is longer than those found in palladium(I) dimers [8]. The average bond length between palladium and C1 and C3 carbons of indenyl rings is 2.175 Å, and that between palladium and C2 carbons is 2.508 Å. Furthermore, the average distance metal–ring-junction carbons is 3.007 Å, which is clearly out of the bonding range. These results indicate the η^3-allyl-ene bonding mode of indenyl groups. The C–C bond distances in the five-membered rings also show evidence of an allyl-ene distortion. It should be noted that, despite these extreme distortion to allyl-ene bonding, distortion of the η^3-In groups from planarity is very small. The average dihedral angle (fold angle) between the η^3-allyl plane and the benzenoid ring is 7° for **3a**, in contrast to that of 26° for $[W(\eta^3\text{-In})(\eta^5\text{-In})(CO)_2]$ [3], 28° for $[Ir(\eta^3\text{-In})(PMe_2Ph)_3]$ [4], or 22° for [Fe(η^3-

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** The notation H1 or C1 represents the standard numbering for the indenyl group.

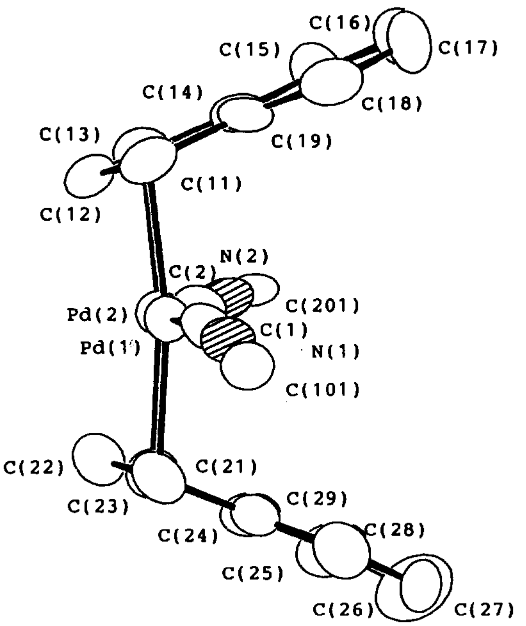

Fig. 2. The wedge-shape arrangement of two η^3-indenyl ligands. Xylyl groups are omitted for clarity.

In)(CO)$_3$]$^-$ [2]. Two indenyl planes lie in a wedge-shape arrangement, the dihedral angle between the two indenyl planes being 48.3(6)° (Fig. 2). The average angle Pd–Pd–C(isocyanide) is 163.7°, showing some distortion from the C–Pd–Pd–C linear arrangement. These structural features are different from those found in the Cp analogue (**1**). To our best knowledge, complex **3** is the first example of η^3-indenyl groups acting as bridging ligands.

Extensive attempts to prepare phosphine and carbonyl complexes having indenyl ligands were carried out. When $PdCl_2(PPh_3)_2$ and [^{n}Bu$_4$N][PdCl$_3$(CO)] were used as starting complexes, no dipalladium compounds with bridging η^3-In were obtained. Thus, the bridging structure with η^3-indenyl groups might be unique to the isocyanide complexes. Further studies including some reactions of complex **3** with small molecules are now in progress.

References and notes

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7 **3a**: UV-Vis (CH_2Cl_2): λ_{max} 418 (ϵ 1.56×10^4 mol^{-1} dm^3 cm^{-1}), and 280 nm (6.07×10^4); IR (nujol), ν(C≡N) 2127 and 2108s cm^{-1}. ^{1}H NMR(CD_3Cl): δ 2.67 (s, *o*-CH$_3$), 4.38 (t, H2 of In), and 6.32 (d, H1, 3 of In). Anal. Found: C, 60.40; H, 4.53; N, 3.94. $C_{36}H_{32}N_2Pd_2$ calc.: C, 61.29; H, 4.57; N, 3.97%. **3b**: UV-Vis (CH_2Cl_2): λ_{max} 417 (ϵ 1.47×10^4 mol^{-1} dm^3 cm^{-1}), and 282 nm (5.94×10^4). IR (nujol): ν(C≡N) 2135 and 2112s cm^{-1}. ^{1}H NMR(CD_3Cl): δ 2.38 (s, *p*-CH$_3$), 2.67 (s, *o*-CH$_3$), 4.42 (t, H2 of

In), and 6.32 (d, H1, 3 of In). Anal. Found: C, 62.31; H, 4.82; N, 3.92. $C_{38}H_{36}N_2Pd_2$ calc.: C, 62.22; H, 4.95; N, 3.82%.

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9 *Crystal data*: $C_{36}H_{32}N_2Pd_2$, $M = 705.5$, monoclinic, space group $P2_1/n$, $a = 19.235(3)$, $b = 9.857(6)$, $c = 15.989(9)$ Å, $\beta = 97.32(3)°$, $U = 3006$ Å^3, $Z = 4$, $D_c = 1.559$ g cm^{-3}, μ(Mo-K_α) = 12.1 cm^{-1}. The structure was solved by direct methods and refined by block-diagonal least-squares techniques to $R = 0.059$ and $R_w = 0.070$, using 3250 unique reflections with $F_o > 5\sigma(F_o)$ measured on an Enraf–Nonius CAD4 diffractometer. An absorption correction was applied. The calculations were carried out on a FACOM M-780 computer with the Universal Computation Program System UNICS III (T. Sakurai and K. Kobayashi, Rikagaku Kenkyusho Hokoku, 55 (1979) 69). Tables of supplementary material are available from the authors.