

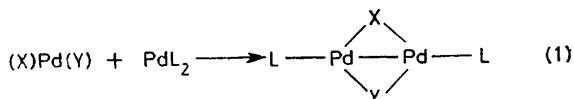
## Di- $\mu$ -(Cyclopentadienyl)-bis(tri-isopropylphosphine)dipalladium(I)

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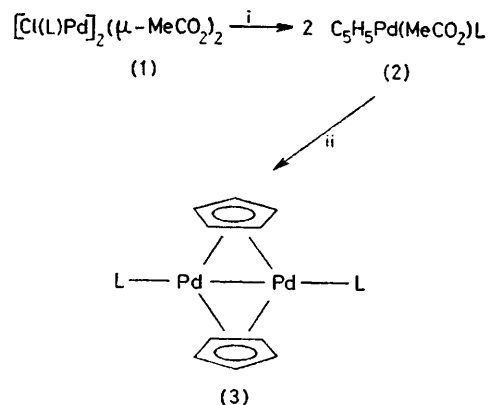
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**Summary** Di- $\mu$ -(cyclopentadienyl)-bis(tri-isopropylphosphine)dipalladium(I) was prepared by the reaction of  $[(C_5H_5)Pd(MeCO_2)(PPr^i_3)]$  with  $NaK_{2.8}$ ; its sandwich-type structure is proved by reactions with  $Me_3SiCl$ ,  $PhSH$ , or  $PhCO_2H$  which give  $[(\mu-C_5H_5)(\mu-X)Pd_2(PPr^i_3)_2]$  ( $X = Cl, PhS, \text{ or } PhCO_2$ ).

BINUCLEAR sandwich-type complexes possessing an  $M_2$  unit co-ordinated by two  $C_nH_n$  ring systems are very rare. Recently, we discovered a simple and straightforward route to obtain (Pd-Pd)-complexes of general composition  $(\mu-X)(\mu-Y)Pd_2L_2$  in which the oxidation state of palladium is +I [equation (1)].<sup>1</sup> The 1+1-addition can be applied to



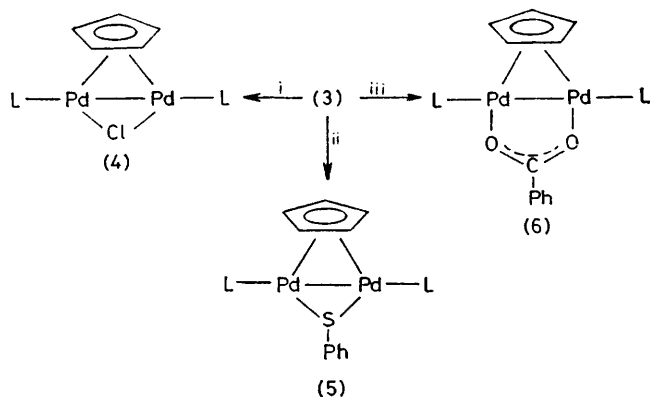
prepare the corresponding complexes with  $X = C_5H_5$ ,  $Y = 2-RC_3H_4$ ;  $X = Y = 2-RC_3H_4$ ;  $X = 2-RC_3H_4$ ,  $Y = Cl, I$ ;<sup>1,2</sup>  $X = 2-RC_3H_4$ ,  $Y = MeCO_2, CF_3CO_2, \text{ or } PhCO_2$ ,<sup>3</sup> and  $L = PPr^i_3, PBu^t_3, \text{ or } P(C_6H_{11})_3$ . There is no possibility, however, of obtaining the binuclear sandwich  $[(\mu-C_5H_5)_2Pd_2L_2]$  according to equation (1) since the necessary starting compound  $Pd(C_5H_5)_2$  has as yet not been prepared.<sup>4</sup>



SCHEME 1. Reagents: i,  $TiC_5H_5$ , THF- $C_6H_6$ , 25 °C, 3 h; ii,  $NaK_{2.8}$ ,  $C_6H_6$ , 25 °C, 5 h ( $L = PPr^i_3$ ).

Therefore, we have used a different route, which is outlined in Scheme 1. The acetate-bridged complex (1)<sup>5</sup> reacts with  $TiC_5H_5$  to give the new mononuclear compound (2) [ $^1H$  n.m.r. ( $C_6D_6$ ):  $\delta$  5.67 (d, 5H,  $J_{PH}$  2.0 Hz) and 2.00 (s, 3H)] which, on treatment with sodium-potassium alloy  $NaK_{2.8}$ ,<sup>6</sup> forms (3) in 55% yield. Compound (3) is also obtained by reaction of  $[(\mu-C_5H_5)(\mu-MeCO_2)Pd_2(PPr^i_3)_2]$ <sup>3</sup>

with excess of  $\text{TiC}_5\text{H}_5$  in benzene. The structure of (3) [ $m/e$  (field desorption) 663.5; calc. 663.5] is confirmed by its  $^1\text{H}$  n.m.r. spectrum which shows a 1:2:1 triplet [ $\delta$  ( $\text{C}_6\text{D}_6$ ) 5.70,  $J_{\text{PH}}$  2.2 Hz] for the cyclopentadienyl protons and excludes the formation of the isomer  $[(\text{C}_5\text{H}_5)(\text{L})\text{Pd}-\text{Pd}(\text{L})-(\text{C}_5\text{H}_5)]$ .<sup>†</sup>



SCHEME 2. Reagents: i,  $\text{Me}_3\text{SiCl}$  (1:1),  $\text{C}_6\text{H}_6$ , 25 °C; ii,  $\text{PhSH}$  (1:1),  $\text{C}_6\text{H}_6$ , 25 °C, 30 min; iii,  $\text{PhCO}_2\text{H}$  (1:1),  $\text{C}_6\text{H}_6$ , 25 °C ( $\text{L} = \text{PPr}^t_3$ ).

There is also strong support for the sandwich-type structure of (3) by its reactions with  $\text{Me}_3\text{SiCl}$ ,  $\text{PhSH}$ , or  $\text{PhCO}_2\text{H}$  (Scheme 2). Compound (4) had originally been prepared by reduction of  $(\text{C}_5\text{H}_5)\text{Pd}(\text{L})\text{Cl}$  with  $\text{Mg}$  or  $\text{LiAlH}(\text{Bu}^t\text{O})_3$  in THF whereas (5) had been obtained by a metathetical reaction of  $[(\mu\text{-C}_5\text{H}_5)(\mu\text{-Br})\text{Pd}_2\text{L}_2]$  and  $\text{TiSPh}$  in benzene.<sup>7</sup> The hitherto unknown complex (6) [ $^1\text{H}$  n.m.r. ( $\text{C}_6\text{D}_6$ ):  $\delta$  5.15 (t,  $J_{\text{PH}}$  2.5 Hz, 5H), 1.22 (d  $\times$  vt 36H),<sup>‡</sup> 8.26 (m, 2H of  $\text{PhCO}_2$ ), and 7.14 (m, 3H of  $\text{PhCO}_2$ )] is an analogue of the above mentioned compound  $[(\mu\text{-C}_5\text{H}_5)(\mu\text{-MeCO}_2)\text{Pd}_2\text{L}_2]$  which is formed by the reaction of  $[(\text{C}_5\text{H}_5)\text{Pd}(\text{MeCO}_2)(\text{C}_6\text{H}_5)]$  and  $\text{PdL}_2$ .<sup>3</sup>

In contrast to  $[(\mu\text{-C}_5\text{H}_5)(\mu\text{-2-Bu}^t\text{C}_3\text{H}_7)\text{Pd}_2\text{L}_2]$ ,<sup>2</sup> complex (3) does not dissociate in solution to give  $\text{Pd}(\text{C}_5\text{H}_5)_2$  and  $\text{PdL}_2$  indicating that co-ordination of two bridging cyclopentadienyl ligands to the  $\text{Pd}_2\text{L}_2$  unit stabilises the binuclear sandwich-type structure.

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<sup>†</sup> See, e.g., the complex  $[(\text{C}_5\text{H}_5)(\text{L})\text{Pd}-\text{Pd}(\text{L})(2\text{-ClC}_3\text{H}_4)]$  which shows a doublet for the cyclopentadienyl protons (ref. 2).

<sup>‡</sup> Doublet of virtual triplets,  $N = {}^3J_{\text{PH}} + {}^6J_{\text{PH}} = \text{ca. } 13.4$ ,  ${}^3J'_{\text{HH}} = 6.7$  Hz.

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