Synthesis of Cyclometallated Naphthylpalladium Complexes *via* Transmetallation Reactions of Naphthylmercury with Palladium Species. Crystal Structure Determination of [$\{Pd(mxn)(O_2CMe)\}_2$][‡]

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The transmetallation reaction of bis(8-dimethylaminonaphthyl)mercury, [$Hg(dman)_2$], with [$PdCl_2(SEt_2)_2$] or [$\{PdCl_2(PPh_3)\}_2$] and palladium acetate afforded, by transfer of the substituted naphthyl group from mercury, a high yield of monoarylated palladium compounds, [Pd(dman)-Cl(L)]. Although no reaction occurred between [$Hg(dman)_2$] and [$PtCl_2(SEt_2)_2$] or [$\{PtCl_2(PEt_3)\}_2$] the reaction between [$Pt(dman)_2$] and $Hg(O_2CMe)_2$ resulted in [$Pt(dman)_2Hg(O_2CMe)_2$] which contains an unsupported Pt–Hg bond. Transmetallation from bis(8-methoxynaphthyl)palladium to [PdL_2Cl_2] [L_2 = cyclo-octa-1,5-diene (cod); L = SEt_2 or PhCN], $Li_2[PdCl_4]$, and HgX_2 (X = O_2CMe or Cl) provided several new arylpalladium complexes originating from exchange of ligands between the metal centres. For one of these products, [$\{Pd(mxn)(O_2CMe)\}_2$] (mxn = 8-methoxynaphthyl), the structure in the solid state was determined by *X*-ray crystallography [monoclinic, space group $P2_1/n$, a = 19.539(2), b = 9.396(2), c = 13.893(3) Å, β = 110.75(1)°]. It shows a dimeric molecule in which the square-planar co-ordinated palladium atoms are bridged by the acetato groups [Pd–O 2.11(1) Å (average)] and each mxn group is *C,O*-chelate bonded to one palladium centre [Pd–C 1.97(2) Å (average), Pd–O 2.10(2) Å(average)]. The molecule is folded such that the Pd ··· Pd distance is 2.842(4) Å with the two naphthyl rings facing each other.

Cyclometallated compounds of platinum(II) and palladium(II) have attracted much interest during the last decade because of their potential utility in the synthesis of organic products.[1] They can be conveniently prepared either by a transmetallation reaction of an organolithium compound and the appropriate metal halide, generally affording disubstituted complexes,[2] or by a direct metallation reaction of the ligand which affords monosubstituted halide-bridged compounds. In particular the latter compounds are of interest, since they show, compared to the disubstituted organopalladium compounds, an enhanced reactivity towards alkynes.[2b,3]

Previously we reported that bis(8-methoxynaphthyl)palladium, [$Pd(mxn)_2$], from the metathetical reaction of palladium halides with [$Li(mxn)]_n$, is a versatile reagent for the synthesis of several organic products.[4] One problem encountered in further research was our inability to obtain compounds of the type [$\{Pd(mxn)X\}_2$] (X = Cl or O_2CMe) *via* direct metallation of Hmxn with $Pd(O_2CMe)_2$ or $Li_2[PdCl_4]$. Therefore, we sought synthetic routes to halide-bridged compounds, based on transmetallation reactions using other organometallic reagents. Recent studies have shown that organomercury and organotin compounds are attractive starting materials for this purpose;[5] because of their lower reactivity compared to that of the corresponding organolithium compounds[6] they generally afford monosubstituted organopalladium compounds. Only a few of such reactions with cyclometallated complexes have been reported;[5s] we have therefore started our study of these transmetallation reactions with the 8-dimethylaminonaphthyl group (dman), a chelating ligand closely related to 8-methoxynaphthyl (mxn). The properties and features of the palladium and platinum complexes with dman are well known.[2b,7,8] It is therefore comparatively easy to interpret the results of transmetallation reactions of this ligand from mercury to platinum and palladium substrates. Subsequently, based on the knowledge gained, synthesis of compounds containing the less well known mxn group can be carried out expeditiously.

Results and Discussion

Starting Compounds.—The novel compounds bis(8-dimethylaminonaphthyl)mercury, [$Hg(dman)_2$], and bis(8-methoxynaphthyl)mercury, [$Hg(mxn)_2$], which were necessary for the transmetallation reactions, could only be prepared by reacting the corresponding aryl-lithium compound Li(dman) and Li(mxn), respectively, with $HgCl_2$ in tetrahydrofuran (thf). The 1:1 reaction of Li(dman) and $HgCl_2$ afforded [Hg(dman)Cl] (**5a**), while the 2:1 reaction affords [$Hg(dman)_2$] (**1**). Unfortunately the analogous reaction of Li(mxn) with $HgCl_2$ did not lead to any stable organomercury compound containing mxn. Transmetallation reactions employing the mxn group were therefore restricted to those of [$Pd(mxn)_2$][9] with metal halide complexes.

Transmetallation Reactions involving the 8-*Dimethylaminonaphthyl Group.*—Treatment of (**1**) with $Pd(O_2CMe)_2$, [$PdCl_2(SEt_2)_2$], and [$\{PdCl_2(PPh_3)\}_2$] in refluxing benzene results in a smooth transfer of one dman group from mercury to palladium and formation of hexane-insoluble naphthylpalladium compounds [Pd(dman)Cl(L)] [L = SEt_2, (**2**); L = PPh_3, (**3**)] and [$\{Pd(dman)(O_2CMe)\}_2$] (**4**) which could be isolated in *ca.* 80% yield (see Scheme 1). These products were easily separated from [Hg(dman)X] (X = Cl or O_2CMe) also

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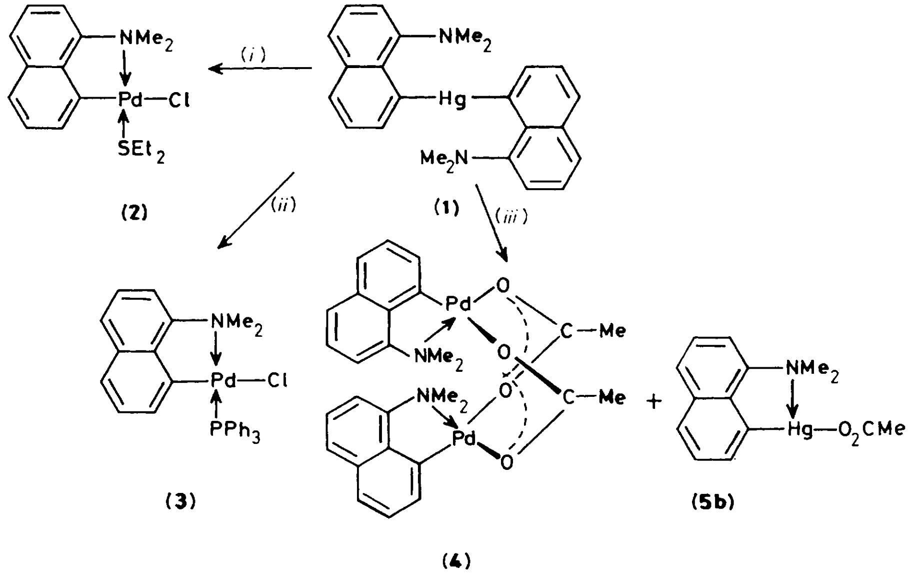
[‡] Di-μ-acetato-*O,O'*-bis[(8-methoxynaphthyl-*C*^{1},*O*)palladium(II)].

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 1. Proton n.m.r. data[a] of the compounds

	Compound	Aryl H	NMe_2/OMe	Other groups
(**1**)	$[Hg(dman)_2]$	7.95—7.20	2.60	
(**2**)	$[Pd(dman)Cl(SEt_2)]$	7.75—7.25	3.46	3.12 (br, 4 H, Et), 1.49 (t, 6 H, J = 7.7 Hz, Et)
(**3**)	$[Pd(dman)Cl(PPh_3)]$	7.91—7.25 6.80—6.50	3.51 (2.5)[b]	
(**4**)	$[\{Pd(dman)(O_2CMe)\}_2]$	7.60—6.90	3.46 (3 H), 2.80 (3 H)	2.34 (3 H, O_2CMe)
(**5a**)	$[Hg(dman)Cl]$	7.90—7.20	2.73	
(**5b**)	$[Hg(dman)(O_2CMe)]$	7.80—7.20	2.75	2.10 (3 H, O_2CMe)
(**6**)	$[Pt(dman)_2Hg(O_2CMe)_2]$	7.70—7.00	3.50 (3 H), 3.18 (3 H)	2.00 (3 H, O_2CMe)
(**8**)	$[Pd(mxn)Cl(SEt_2)]$	7.66—6.69	4.27	2.65 (q, 4 H, Et), 1.29 (t, 6 H, Et)
(**9**)	$[Pd_2(mxn)_3Cl]$	7.50—6.63, 6.20 (t, 1 H), 5.40 (dd, 1 H)	4.58 (3 H), 4.25 (3 H), 3.72 (3 H)	
(**10**)	$[Pd(mxn)Cl(cod)]$	7.71—6.74	3.91	6.50 (2 H, dd), 6.00 (2 H, dd) (CH=CH, cod) 2.60, 2.30 (CH_2-CH_2, cod)
(**11**)	$[\{Pd(mxn)(O_2CMe)\}_2]$	7.54—6.76	4.07 (3 H)	2.14 (3 H, O_2CMe)
(**12**)	$[Pd(mxn)Cl(SEt_2)_2]$	7.51—6.71	4.15 (3 H)	2.60 (q, 8 H, Et), 1.30 (t, 12 H, Et)

[a] Relative to $SiMe_4$, recorded in $CDCl_3$. [b] $^4J(^{31}P^1H)$ in parentheses.



Scheme 1. (*i*) $[PdCl_2(SEt_2)_2]$, refluxing benzene, 24 h; (*ii*) $[\{PdCl_2(PPh_3)\}_2]$, refluxing benzene, 24 h; (*iii*) $Pd(O_2CMe)_2$, refluxing benzene, 24 h

formed in the reaction by virtue of the good hexane solubility of the latter. The identity of [Hg(dman)X] was established by comparison of ^1H n.m.r. spectra with an authentic sample of [Hg(dman)X]. The [Pd(dman)X(L)] complexes were characterized by ^1H n.m.r. (see Table 1), field desorption (f.d.) mass spectrometry, and elemental analysis.

Of these products the acetato-bridged dimer $[\{Pd(dman)(O_2CMe)\}_2]$ (**4**) can in principle exist in either a *cis* or a *trans* isomeric form (see Figure 1). However the 100-MHz ^1H n.m.r. spectrum of isolated (**4**) shows two signals for the diastereotopic NMe_2 methyl groups and only one signal for the acetato bridge indicative of only one isomer, *i.e. trans* (for a more detailed discussion of the n.m.r. spectra of this type of compound see ref. 10). For the *cis* isomer one would observe two signals for the acetato groups. The *trans* geometry seems to be the most common for this type of complex.[11–14]

In the ^1H n.m.r. spectrum of $[Pd(dman)Cl(PPh_3)]$ (**3**), synthesized previously,[8] the NMe_2 protons show a small ^{31}P

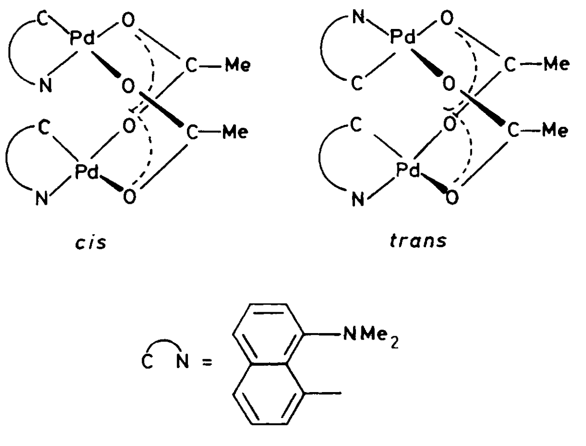


Figure 1. *cis* and *trans* isomers of $[\{Pd(dman)(O_2CMe)\}_2]$ (**4**)

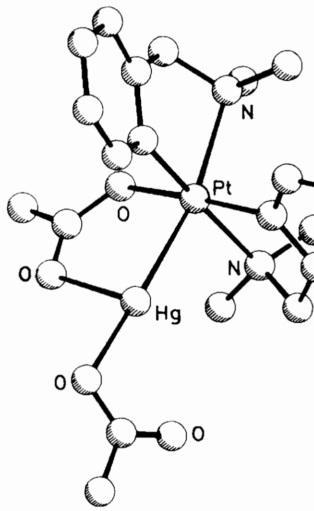
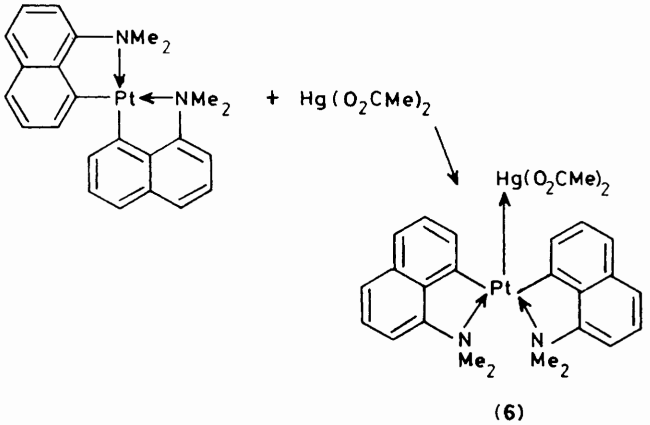
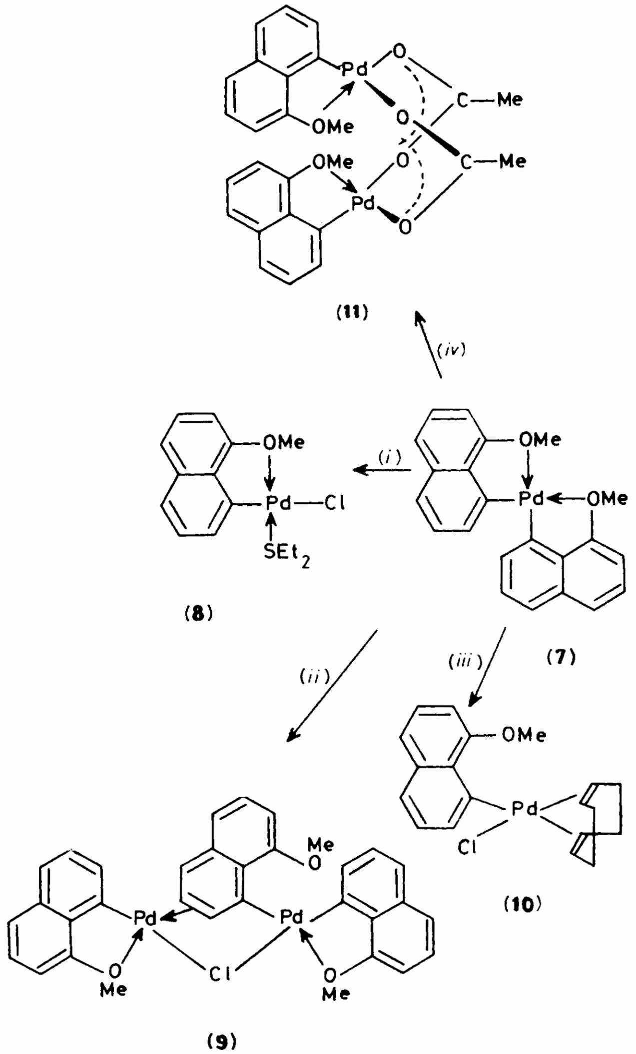


Figure 2. Molecular structure of $[(2\text{-}Me_2NCH_2C_6H_4)_2(O_2CMe)PtHg(O_2CMe)]$



Scheme 2.



Scheme 3. (*i*) $[PdCl_2(SEt_2)_2]$, Et_2O, 0 °C; (*ii*) $Li_2[PdCl_4]$, thf, −70 °C; (*iii*) $[PdCl_2(cod)]$ (cod = cyclo-octa-1,5-diene), thf, room temperature; (*iv*) $Hg(O_2CMe)_2$, toluene, reflux

coupling of 2.5 Hz which is in agreement with the reported value. On the basis of this coupling a *trans* Pd–NMe_2 to Pd–PPh_3 geometry was proposed and, consequently, the Pd–Cl and Pd–C bonds are also *trans* positioned. On the basis of results from earlier stereochemical studies this seems to be the common geometry and is, therefore, also proposed for $[Pd(dman)Cl(SEt_2)]$ (**2**) (see Scheme 1).

There was no reaction between $[Hg(dman)_2]$ and either $[PtCl_2(SEt_2)_2]$ or $[\{PtCl_2(PEt_3)\}_2]$ under the same conditons used for the palladium compounds described above. However, treatment of *cis*-$[Pt(dman)_2]$[7] with $Hg(O_2CMe)_2$ afforded a new dimetallic compound that analysed as $[Pt(dman)_2Hg(O_2CMe)_2]$. Its 100 MHz ^1H n.m.r. spectrum showed two different NMe_2 methyl groups while the isochronous acetato signal is consistent with equivalent acetato methyl groups. The presence of a ^{195}Pt coupling on both of the NMe_2 proton signals indicates a stable Pt–N co-ordination in solution on the n.m.r. time-scale. From these observations a square-pyramidal structure with an apical, unsupported Pt–Hg bond is proposed (see Scheme 2).

Support for this proposal comes from a number of other studies. First a species with a similar Pt–Hg bond has been observed before in the reaction of $Hg(O_2CR)_2$ (R = Me or Pr^i) with *trans*-$[Pt(C_6H_4CH_2NMe_2\text{-}2)_2]$,[15] although, in a subsequent reaction, the Pt^{IV} species $[Pt(C_6H_4CH_2NMe_2\text{-}2)_2(O_2CMe)_2]$ and Hg^0 were formed. However, stable Pt–Hg bonded compounds $[\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(RCO_2)PtHg(O_2CR)X]$ (X = Br or O_2CR; R = Me or Pr^i) have been shown to result from the reaction of $Hg(O_2CR)_2$ with $[PtX\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ (X = Br or O_2CR), containing a tridentate ligand that enforces a fixed *trans* N–Pt–N arrangement. Secondly, the reaction of $Hg(O_2CR)_2$ with *cis*-$[Pt(C_6H_4CH_2NMe\text{-}2)_2]$, in contrast to that with *trans*-$[Pt(C_6H_4CH_2NMe\text{-}2)_2]$ affords a dinuclear octahedral complex with a Pt–Hg bond and one carboxylato group bridging between the two metallic centres (see Figure 2).[15] This latter type of complex can, however, be excluded for $[Pt(dman)_2Hg(O_2CMe)_2]$, since this would give rise to four signals for the NMe_2 methyl groups and two acetato signals in the ^1H n.m.r. spectrum. Finally there is a precedent for a compound with an unsupported Pt–metal bond in $[(C_4H_8S)(C_6F_5)_3PtAg(PPh_3)]$ whose structure was elucidated by *X*-ray diffraction analysis.[16]

The reactivity of $Hg(O_2CR)_2$ with *cis*-$[Pt(dman)_2]$ affording the unsupported dimetallic compound is clearly different from that with *cis*-$[Pt(C_6H_4CH_2NMe_2\text{-}2)_2]$ affording a dinuclear octahedral complex. A reasonable explanation for this different reactivity of $[Pt(dman)_2]$ might be found in the rigidity of the naphthyl skeleton which inevitably keeps the dimethylamino group in the co-ordination sphere of the platinum atom. In the case of $[Pt(C_6H_4CH_2NMe_2\text{-}2)_2]_2]$ the formation of a carboxylato-bridged dimer (Figure 2)[15] needs a rearrangement of the cyclometallated ligands probably involving de-co-ordination of one of the NMe_2 groups. This latter process seems very unlikely for $[Pt(dman)_2]$ with its rigid five-membered chelate rings, and consequently only complexation of $Hg(O_2CR)_2$ with $[Pt(dman)_2]$ occurs, the rearrangement to an acetato-bridged structure being blocked.

Transmetallation involving the 8-*Methoxynaphthyl Group*.—Since methoxynaphthyl mercury compounds could not be synthesized, only $[Pd(mxn)_2]$ was available as transmetallating agent. Scheme 3 summarizes the transmetallation reactions of this compound with several palladium salts. With $[PdCl_2(SEt_2)_2]$ in toluene it smoothly affords the mono-naphthyl compound $[Pd(mxn)Cl(SEt_2)]$ (**8**), whose 200-MHz ^1H n.m.r. spectrum showed an OMe resonance at 4.27 p.p.m. indicative of the presence of a chelating mxn group.[9] It is not possible to obtain this product *via* the usual route of Li(mxn) and $[PdCl_2(SEt_2)_2]$ as this reaction affords $[Pd(mxn)Cl(SEt_2)_2]$ (**12**). The identification of (**12**) is based on its elemental analysis and its ^1H n.m.r. spectrum which is similar to that of the Pt analogue.[7] In solution at 0 °C $[Pd(mxn)Cl(SEt_2)_2]$ decomposes quickly to the C–C coupled binaphthyl $(mxn)_2$ and Pd^0.* Since this decomposition is also observed for other Pd–mxn compounds in solution[4] it is necessary to isolate them quickly after their formation. The exact route for the decomposition is unknown. Mono-arylated [Pd(mxn)Cl(cod)] (**10**) (cod = cyclo-octa-1,5-diene) could be obtained *via* the reaction of $[Pd(mxn)_2]$ with $[PdCl_2(cod)]$ in thf. The ^1H n.m.r. spectrum of (**10**) shows the OMe signal at 3.91 p.p.m. in accordance with a non-co-ordinated OMe group.[9] When $[Pd(mxn)_2]$ was reacted with $[PdCl_2(cod)]$ in diethyl ether instead of thf a rather unusual compound with stoicheiometry $[Pd_2(mxn)_3Cl]$ (**9**) was formed indicating an important influence of the solvent on the products formed. This species was also obtained from the reaction of $[Pd(mxn)_2]$ with $Li_2[PdCl_4]$, $[PdCl_2(PhCN)_2]$, or $HgCl_2$ in diethyl ether.

Despite the instability of (**9**) in $CDCl_3$ solution† it was possible to run an ^1H n.m.r. spectrum of the compound. This showed three OMe signals, indicating the presence of three different mxn groups, together with signals at 6.20 and 5.40 p.p.m. attributed to shielded naphthyl protons. The ^1H n.m.r. spectral features of (**9**) bear some analogy to those of $[\{NC_9H_6CH_2C(CF_3){=}C(CF_3)\}Pd\{C(CF_3){=}C(CF_3)C_{10}H_6OMe\}]$, for which an *X*-ray crystal structure has been determined[17] (see Figure 3). On this basis, although the characterization is not complete, we propose for (**9**) the structure depicted in Scheme 3 containing an η^2 interaction of the naphthyl skeleton of one of the mxn groups to palladium.

In the reaction of $Hg(O_2CMe)_2$ with $[Pd(mxn)_2]$ an acetato-bridged dimer $[\{Pd(mxn)(O_2CMe)\}_2]$ (**11**) is formed, together with some $(mxn)_2$. This binaphthyl is always formed in reactions of $[Pd(mxn)_2]$ and it is not known whether it is a reaction by-product or whether it originates from partial thermal decomposition of $[Pd(mxn)_2]$. From the ^1H n.m.r. spectrum of (**11**), which showed one resonance pattern for the mxn groups and one acetato signal, it can be concluded that in solution (as in the solid state, see below) it is solely the *trans* isomer that is present. In particular the high-field shift of the co-ordinated OMe groups is consistent with the weak *trans* influence of the opposite oxygen donor of the acetato group.

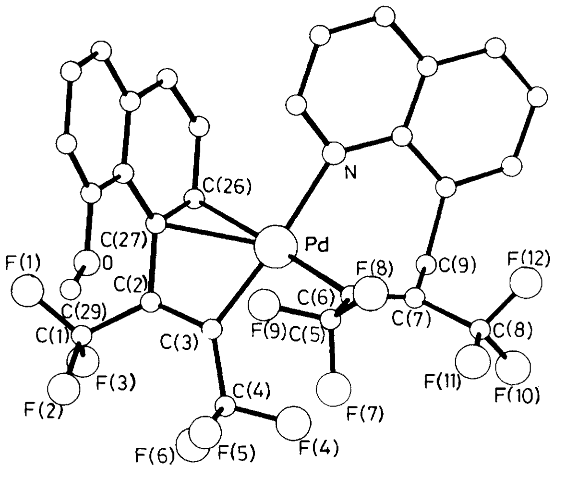


Figure 3. Molecular structure of $[\{NC_9H_6CH_2C(CF_3){=}C(CF_3)\}Pd\{C(CF_3){=}C(CF_3)C_{10}H_6OMe\}]$ showing the π interaction of the methoxynaphthyl group [*via* C(27)–C(26)] with palladium

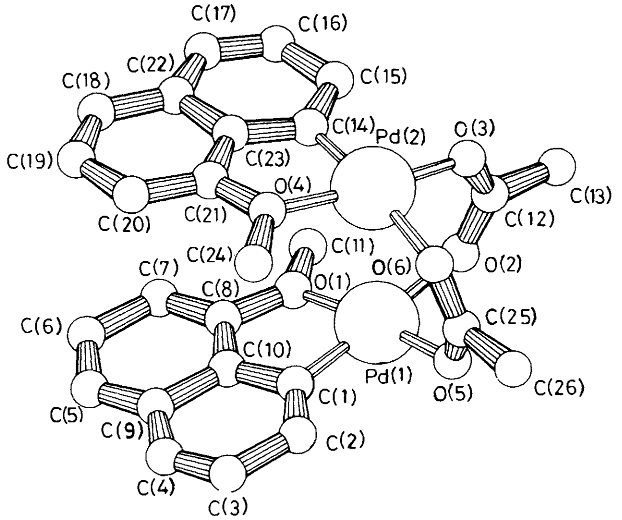


Figure 4. Molecular structure of $[\{Pd(mxn)(O_2CMe)\}_2]$ (**11**)

The molecular geometry of (**11**) is shown in Figure 4, along with the adopted numbering scheme. Relevant bond distances and angles are shown in Table 2. The molecule is a dimer in which one mxn group is chelated to each palladium atom with the two Pd atoms being bridged by two mutually perpendicular acetato groups. Each Pd atom thus has a slightly distorted square-planar co-ordination geometry, comprising two *cis* positioned oxygen atoms of the acetato bridges and the C–O chelate of the mxn group. The most significant deviation from an ideal square-planar geometry results from the bite angle of the mxn group [O–Pd–C 81(1)°]. The Pd–C distances [1.97(3) Å] are normal for this type of compound.[18–21] The two metal co-ordination planes, which contain the two planar mxn groups are held virtually parallel as a result of the bite of the acetato bridges. The Pd $\cdots$ Pd distance of 2.842(4) Å is in the range found for other acetato-bridged complexes, and is usually regarded as non-bonding.[11–14]

It is now well established that the interaction of cyclometallated platinum or palladium compounds with

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* Although several experiments were carried out to elucidate the mechanism of this coupling reaction starting from a mono-naphthyl palladium species no conclusive information could be obtained. All attempts to identify a free radical mechanism failed. Since binaphthyl is the only product observed in this reaction the decomposition probably proceeds *via* a dinuclear intermediate (see ref. 4).

† After leaving (**9**) in $CDCl_3$ for 1 h, ^1H n.m.r. spectroscopy showed only signals attributable to $(mxn)_2$ and solvent.

Table 2. Bond distances (Å) and angles (°)

Pd(1)–Pd(2)	2.842(4)	C(2)–C(3)	1.43(4)	O(1)–C(11)	1.46(4)	C(18)–C(19)	1.34(5)
Pd(1)–C(1)	1.97(3)	C(3)–C(4)	1.34(4)	C(12)–O(2)	1.26(4)	C(19)–C(20)	1.51(5)
Pd(1)–O(1)	2.11(2)	C(4)–C(9)	1.37(4)	C(12)–O(3)	1.17(4)	C(20)–C(21)	1.40(5)
Pd(1)–O(2)	2.17(2)	C(9)–C(10)	1.45(4)	C(12)–C(13)	1.54(5)	C(21)–C(23)	1.36(4)
Pd(1)–O(5)	2.04(2)	C(9)–C(5)	1.45(5)	C(14)–C(15)	1.33(5)	C(21)–O(4)	1.38(3)
Pd(2)–C(14)	1.97(3)	C(5)–C(6)	1.38(6)	C(15)–C(16)	1.47(4)	C(24)–O(4)	1.46(4)
Pd(2)–O(3)	2.09(2)	C(6)–C(7)	1.42(5)	C(16)–C(17)	1.28(5)	C(25)–O(5)	1.24(4)
Pd(2)–O(4)	2.10(2)	C(7)–C(8)	1.44(4)	C(17)–C(22)	1.42(5)	C(25)–O(6)	1.25(3)
Pd(2)–O(6)	2.14(2)	C(8)–C(10)	1.41(4)	C(22)–C(23)	1.49(4)	C(25)–C(26)	1.51(4)
C(1)–C(2)	1.40(4)	C(8)–O(1)	1.34(4)	C(22)–C(18)	1.37(5)		
C(1)–Pd(1)–Pd(2)	99(2)	C(1)–C(2)–C(3)	114(2)	C(14)–Pd(2)–Pd(1)	105(1)	C(14)–C(15)–C(16)	120(3)
O(1)–Pd(1)–Pd(2)	94(1)	C(2)–C(3)–C(4)	124(3)	O(4)–Pd(2)–Pd(1)	96(1)	C(15)–C(16)–C(17)	121(3)
O(2)–Pd(1)–Pd(2)	77(1)	C(3)–C(4)–C(9)	124(3)	O(3)–Pd(2)–Pd(1)	85(1)	C(16)–C(17)–C(22)	125(3)
O(5)–Pd(1)–Pd(2)	86(1)	C(4)–C(9)–C(10)	116(3)	O(6)–Pd(2)–Pd(1)	76(1)	C(17)–C(22)–C(23)	114(3)
C(1)–Pd(1)–O(1)	81(1)	C(4)–C(9)–C(5)	130(3)	C(14)–Pd(2)–O(4)	83(1)	C(17)–C(22)–C(18)	128(3)
C(1)–Pd(1)–O(2)	174(1)	C(9)–C(5)–C(6)	124(3)	C(14)–Pd(2)–O(3)	91(1)	C(22)–C(18)–C(19)	123(3)
C(1)–Pd(1)–O(5)	91(1)	C(5)–C(6)–C(7)	121(3)	C(14)–Pd(2)–O(6)	176(1)	C(18)–C(19)–C(20)	122(3)
O(1)–Pd(1)–O(2)	95(1)	C(6)–C(7)–C(8)	117(3)	O(4)–Pd(2)–O(3)	174(1)	C(19)–C(20)–C(21)	113(3)
O(1)–Pd(1)–O(5)	173(1)	C(7)–C(8)–C(10)	121(3)	O(4)–Pd(2)–O(6)	94(1)	C(20)–C(21)–C(23)	126(3)
O(2)–Pd(1)–O(5)	93(1)	C(8)–C(10)–C(9)	122(3)	O(3)–Pd(2)–O(6)	92(1)	C(21)–C(23)–C(22)	118(2)
Pd(1)–O(1)–C(8)	113(2)	C(8)–C(10)–C(1)	119(3)	Pd(2)–O(4)–C(21)	111(2)	C(21)–C(23)–C(14)	123(2)
Pd(1)–O(1)–C(11)	126(2)	C(10)–C(9)–C(5)	114(3)	Pd(2)–O(4)–C(24)	123(2)	C(23)–C(22)–C(18)	118(3)
Pd(1)–O(2)–C(12)	126(2)	C(8)–O(1)–C(11)	120(2)	Pd(2)–O(3)–C(12)	121(2)	C(21)–O(4)–C(24)	126(2)
Pd(1)–O(5)–C(25)	122(2)	O(2)–C(12)–O(3)	129(3)	Pd(2)–O(6)–C(25)	130(2)	O(5)–C(25)–O(6)	124(2)
Pd(1)–C(1)–C(2)	125(2)	O(2)–C(12)–C(13)	117(3)	Pd(2)–C(14)–C(15)	130(2)	O(5)–C(25)–C(26)	121(3)
Pd(1)–C(1)–C(10)	112(2)	O(3)–C(12)–C(13)	114(3)	Pd(2)–C(14)–C(23)	109(2)	O(6)–C(25)–C(26)	115(3)

mercury carboxylates can result in either the direct formation of stable dinuclear compounds, or the formation of products *via* transmetallation or oxidative addition reactions.[5a] In the last two the initial formation of an unstable or transient dinuclear species was postulated. The products found from the reaction of [Hg(dman)$_2$] and Pd(O$_2$CMe)$_2$ [see Scheme 4] can be accounted for by elimination of [Hg(dman)(O$_2$CMe)] with concomitant formation of [{Pd(dman)(O$_2$CMe)}$_2$]. The reaction of [Pd(mxn)$_2$] and Hg(O$_2$CMe)$_2$ is likely to involve a similar mechanism but since it was not possible unambiguously to establish the origin of (mxn)$_2$ in this reaction it has not been possible to prove this.

$$\begin{aligned}&[\mathrm{Hg(dman)_2}] + \mathrm{Pd(O_2CMe)_2} \longrightarrow\\ &\qquad [\mathrm{(O_2CMe)_2Pd\{Hg(dman)_2\}}] \longrightarrow\\ &\qquad [\{\mathrm{Pd(dman)(O_2CMe)}\}_2] + [\mathrm{Hg(dman)(O_2CMe)}]\end{aligned}$$

Scheme 4.

Conclusions

Transmetallation from cyclometallated mercury and palladium compounds to palladium salts is a useful route to [{Pd(mxn)X}$_2$] products which are either not available *via* a metathetical reaction with organolithium compounds, or are not accessible *via* direct metallation. The new compounds are thermally unstable and a study of the high reactivity of some of them is currently in progress.

Experimental

Syntheses were carried out with standard Schlenk techniques in an atmosphere of purified nitrogen. The solvents were dried and distilled prior to use. The following compounds were prepared by reported methods: [Li(dman)·Et$_2$O]$_2$,[22] [PtCl$_2$(SEt$_2$)$_2$],[23] [PtCl$_2$(cod)],[24] [{PtCl$_2$(PEt$_3$)}$_2$],[25] [{PdCl$_2$(PPh$_3$)}$_2$],[26] [PdCl$_2$(cod)],[27] [PdCl$_2$(PhCN)$_2$],[28] [Pt(dman)$_2$],[7] and [Pd(mxn)$_2$].[9]

Proton n.m.r. spectra were obtained on Bruker AC 100 and Bruker WM 250 spectrometers. The field desorption mass spectra (f.d.m.s.) were obtained with a Varian MAT 711 double focussing mass spectrometer with a combined electron impact/field ionization/field desorption source. Tungsten wire f.d. emitters (10 μm) containing carbon micro-needles with an average length of 30 μm were used. The samples were dissolved in chloroform and then loaded onto the emitter by the dipping technique.[29] The emitter currents used to desorb the samples are given in parentheses. The ion source temperature was generally 80 °C. Elemental analyses were obtained from the section Elemental Analyses of ITC Zeist, The Netherlands, and from the Service de Microanalyses du C.N.R.S., Lyon, France.

Synthesis of Bis(8-dimethylaminonaphthyl)mercury, (**1**).—A solution of HgCl$_2$ (0.8 g, 3 mmol) in thf (10 cm^3) was added to a solution of Li(dman)·Et$_2$O (1.5 g, 6.0 mmol) in thf (40 cm^3). The grey-white suspension was stirred overnight and subsequently evaporated to dryness. The resulting off-white residue was extracted with boiling benzene (150 cm^3) (filtration of the solution through Celite was sometimes necessary to remove finely divided LiCl). Removal of the benzene *in vacuo* afforded a white powder which was washed with diethyl ether. Yield: 1.8 g (80%) (Found: C, 53.35; H, 4.50; N, 5.20. Calc. for C$_{24}$H$_{24}$HgN$_2$: C, 53.3; H, 4.45; N, 5.20%). F.d.m.s. (10 mA, CHCl$_3$): *m/e* 540. Calc. for C$_{24}$H$_{24}$HgN$_2$, 540.

Transmetallation of [Hg(dman)$_2$] *with* [{PdCl$_2$(PPh$_3$)}$_2$] *and* [PdCl$_2$(SEt$_2$)$_2$].—Equimolar amounts (0.5 mmol scale) of [Hg(dman)$_2$] and either [{PdCl$_2$(PPh$_3$)}$_2$] or [PdCl$_2$(SEt$_2$)$_2$] were mixed in benzene (75 cm^3) and refluxed for 24 h. The light yellow solution was cooled to room temperature, filtered through Celite and subsequently evaporated to dryness. The residue was washed three times with hexane (15 cm^3) and dried *in vacuo*, to afford the light yellow palladium compounds (**2**) and (**3**) in 85—90% yields. Evaporation of the combined hexane washings afforded [Hg(dman)Cl] [Found for (**3**): C, 62.45; H, 4.75; N, 2.25; P, 5.30. Calc. for C$_{30}$H$_{27}$ClNPPd: C, 62.7; H, 4.75; N, 2.45; P, 5.40%]. F.d.m.s. (10—12 mA, CHCl$_3$): *m/e* 573. Calc.

Table 3. Atomic fractional co-ordinates

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pd(1)	0.452 5(1)	0.083 0(2)	0.161 2(2)	O(3)	0.362(1)	0.237(1)	0.301(2)
Pd(2)	0.325 8(1)	0.051 1(3)	0.214 8(2)	C(14)	0.248(2)	0.156(3)	0.108(3)
C(1)	0.444(2)	−0.094(3)	0.082(2)	C(15)	0.228(2)	0.292(4)	0.106(3)
C(2)	0.475(1)	−0.225(3)	0.123(2)	C(16)	0.168(2)	0.345(4)	0.016(3)
C(3)	0.459(2)	−0.338(4)	0.049(3)	C(17)	0.138(2)	0.265(4)	−0.063(3)
C(4)	0.419(2)	−0.323(4)	−0.050(3)	C(18)	0.120(2)	0.026(4)	−0.148(3)
C(5)	0.340(2)	−0.167(5)	−0.198(3)	C(19)	0.143(2)	−0.109(4)	−0.148(3)
C(6)	0.311(2)	−0.034(4)	−0.232(3)	C(20)	0.199(2)	−0.176(4)	−0.053(3)
C(7)	0.328(2)	0.086(4)	−0.165(2)	C(21)	0.230(1)	−0.078(3)	0.026(2)
C(8)	0.375(1)	0.062(3)	−0.060(2)	C(22)	0.152(2)	0.118(4)	−0.068(3)
C(9)	0.388(2)	−0.197(3)	−0.093(2)	C(23)	0.212(1)	0.062(3)	0.025(2)
C(10)	0.403(2)	−0.075(3)	−0.025(2)	C(24)	0.302(2)	−0.270(4)	0.148(3)
C(11)	0.366(2)	0.307(3)	−0.012(2)	C(25)	0.475(1)	−0.079(3)	0.348(2)
C(12)	0.409(2)	0.306(3)	0.292(2)	C(26)	0.517(2)	−0.163(4)	0.443(3)
C(13)	0.423(2)	0.447(4)	0.353(3)	O(4)	0.282(1)	−0.123(2)	0.118(1)
O(1)	0.394(1)	0.163(2)	0.013(2)	O(5)	0.507(1)	−0.020(2)	0.296(2)
O(2)	0.449(1)	0.281(2)	0.239(2)	O(6)	0.407(1)	−0.075(2)	0.326(1)

for $C_{30}H_{27}ClNPPd$, 573. [Found for (**2**): C, 47.5; H, 5.55; Cl, 8.90; N, 3.45. Calc. for $C_{16}H_{22}ClNPdS$: C, 47.75; H, 5.50; Cl, 8.80; N, 3.50%]. F.d.m.s. (25 mA, $CHCl_3$): *m/e* 401. Calc. for $C_{16}H_{22}ClNPdS$, 401. [Found for (**5a**): C, 35.45; H, 3.20; N, 3.35. Calc. for $C_{12}H_{12}ClHgN$: C, 35.45; H, 3.00; N, 3.45%].

Transmetallation of [Hg(dman)$_2$] *with* Pd(O_2CMe)$_2$.—[Hg(dman)$_2$] (0.46 g, 0.85 mmol) and Pd(O_2CMe)$_2$ (0.18 g, 0.85 mmol) in benzene (50 cm^3) were refluxed for 24 h. The light yellow solution was evaporated to dryness and the resulting residue was recrystallized from CH_2Cl_2–hexane to afford yellow [{Pd(dman)(O_2CMe)}$_2$] (**4**). Yield: 0.45 g (80%). Removal of the solvent from the mother-liquor *in vacuo* afforded a colourless oil which, based on its 100-MHz ^{1}H n.m.r. spectral data, appeared to be [Hg(dman)(O_2CMe)] (Found: C, 49.95; H, 4.70; N, 3.90; O, 9.20. Calc. for $C_{14}H_{15}NO_2Pd$: C, 50.1; H, 4.50; N, 4.15; O, 9.55%). F.d.m.s. (5 mA, $CHCl_3$): *m/e* 672. Calc. for the dimer, 670.

Reaction of [Pt(dman)$_2$] *with* Hg(O_2CMe)$_2$.—To a solution of [Pt(dman)$_2$] (270 mg, 0.62 mmol) in CH_2Cl_2 (10 cm^3) was added Hg(O_2CMe)$_2$ (200 mg, 0.62 mmol). The resulting solution was stirred for 15 min. Evaporation of the solvent and addition of hexane to the residue afforded a pale yellow compound which was filtered off and dried *in vacuo*. Yield of compound (**6**): 0.38 g (80%) (Found: C, 38.95; H, 3.60; N, 3.20; O, 7.30. Calc. for $C_{28}H_{30}HgN_2O_4Pt$: C, 39.35; H, 3.55; N, 3.30; O, 7.50%). F.d.m.s. (10 mA, $CHCl_3$): *m/e* 854. Calc. for $C_{28}H_{30}HgN_2O_4Pt$, 853.

Synthesis of Chloro(*diethyl sulphide*)(8-*methoxynaphthyl*)-*palladium*(II), (**8**).—[PdCl$_2$(SEt$_2$)$_2$] (0.178 g, 0.5 mmol) in diethyl ether (20 cm^3) was added to a solution of [Pd(mxn)$_2$] (0.210 g, 0.5 mmol) in diethyl ether (20 cm^3) at 0 °C. The solution turned bright yellow and after 15 min the yellow compound (**8**) precipitated from the solution. The precipitate was filtered off, washed with diethyl ether and then dried *in vacuo* to afford yellow (**8**). Yield: 0.224 g (58%) (Found: C, 45.85; H, 4.95. Calc. for $C_{15}H_{19}ClOPdS$: C, 46.3; H, 4.90%).

Synthesis of μ-*Chloro-tris*(8-*methoxynaphthyl*)*dipalladium*(II) (**9**).—To a solution of [Pd(mxn)$_2$] (0.210 g, 0.5 mmol) in thf (20 cm^3) was added a solution of Li$_2$[PdCl$_4$] (0.131 g, 0.5 mmol, carefully dried) in thf (20 cm^3) at −70 °C. The violet reaction mixture was allowed to attain room temperature and the solution was then filtered through a layer of Al_2O_3 (5 cm). The violet filtrate was concentrated *in vacuo* to *ca.* 20 cm^3 and pentane (25 cm^3) was added. Standing overnight at −20 °C afforded violet crystals of (**9**). Yield: 0.035 g (10%) (Found: C, 54.90; H, 4.10. Calc. for $C_{33}H_{27}ClO_3Pd_2$: C, 55.05; H, 3.80%).

The reaction of [Pd(mxn)$_2$] with [PdCl$_2$(cod)], [PdCl$_2$(PhCN)$_2$], and HgCl$_2$ was carried out similarly in diethyl ether using the method described above.

Synthesis of Chloro(*cyclo-octa*-1,5-*diene*)(8-*methoxynaphthyl*)*palladium*(II), (**10**).—A solution of [PdCl$_2$(cod)] (0.143 g, 0.5 mmol) in thf (15 cm^3) was added to a solution of [Pd(mxn)$_2$] (0.120 g, 0.5 mmol) in thf (30 cm^3). A violet solution was formed immediately and subsequently a black material precipitated. The solution was quickly filtered and pentane (90 cm^3) added to the filtrate resulting in the formation of a brown precipitate and a yellow solution. This mixture was filtered and the yellow filtrate was stored at −20 °C for two days, affording yellow crystalline (**10**). Yield: 0.065 g (16%) (Found: C, 56.45; H, 5.45. Calc. for $C_{19}H_{21}ClOPd$: C, 56.05; H, 5.20%).

Synthesis of Di-μ-*acetato-bis*[(8-*methoxynaphthyl*)*palladium*(II)], (**11**).—To a toluene solution (30 cm^3) containing [Pd(mxn)$_2$] (0.200 g, 0.47 mmol) was added a solution of Hg(O_2CMe)$_2$ (0.151 g, 0.47 mmol). The resulting yellow solution was refluxed for 15 min after which pentane (70 cm^3) was added. The solution was left overnight at −20 °C giving yellow crystals of (**11**). Yield: 0.160 g (26%) (Found: C, 47.95; H, 3.80. Calc. for $C_{13}H_{12}O_3Pd$: C, 48.4; H, 3.75%).

Synthesis of Chlorobis(*diethyl sulphide*)(8-*methoxynaphthyl*)-*palladium*(II), (**12**).—To a solution of [PdCl$_2$(SEt$_2$)$_2$] (2.12 g, 5.93 mmol) in thf (35 cm^3) at 0 °C was added a solution containing Li(mxn) (1.468 g, 8.9 mmol) in thf (70 cm^3). The resulting orange-red solution was stirred for 5 min and filtered through Al_2O_3 which was prewashed with thf. Subsequently the solution was evaporated to dryness and the residue obtained was redissolved in thf (30 cm^3). Addition of pentane (70 cm^3) to this solution afforded a yellow-orange precipitate which was filtered off and dried *in vacuo*. Yield: 0.69 g (25%). A second fraction could be obtained by leaving the mother-liquor at −20 °C for 1 d. Total yield: 1.09 g (39%) (Found: C, 47.7; H, 5.90. Calc. for $C_{19}H_{29}ClOPdS_2$: C, 47.6; H, 6.00%).

Crystal Structure Determination of (**11**).—*Crystal data.* $C_{26}H_{24}O_6Pd_2$, *M* = 645.32, monoclinic, space group $P2_1/n$, unit-cell dimensions $a = 19.539(2)$, $b = 9.396(2)$, $c = 13.893(3)$ Å, $\beta = 110.75(1)°$, $Z = 4$, $D_c = 1.08$ g cm^{-3}, $\mu = 15.27$ cm^{-1}, $F(000) = 1\,280$; crystal dimensions 0.25 × 0.22 × 0.075 mm. 4 454 Independent intensities were measured on a Nonius CAD4 diffractometer using graphite-monochromated Mo-K_α radiation ($\lambda = 0.710\,69$ Å); 3 165 of these were below the $3\sigma(I)$ level and were treated as unobserved.

The Pd atoms were derived from a Patterson synthesis and C and O were found from a subsequent ΔF synthesis. After isotropic block-diagonal least-squares refinement an empirical absorption correction (DIFABS[30]) was applied. Continued refinement, anisotropic for Pd and isotropic for C and O, converged to $R = 0.074$ ($R' = 8.5$). The anomalous dispersion of Pd was taken into account and a weighting scheme $w = 1/(4.72 + F_o + 0.06F_o^2)$ was applied.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond distances and angles.

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