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Preliminary communication

Convenient synthetic routes to $MePd^{II}$, Me_2Pd^{II}, and Me_3Pd^{IV} complexes. The crystal structure of the $MePd^{II}$ complex [MePd(2,2′-bipyridyl)(γ-picoline)]BF_4

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Abstract

The pyridazine complex $[Me_2Pd(pyd)]_n$, stable as a solid on storage at ca. −20 °C and obtained on reaction of *trans*-$PdCl_2(SMe_2)_2$ with methyllithium and pyridazine at low temperature, is an excellent precursor for the synthesis of Me_2Pd^{II} and Me_3Pd^{IV} complexes under mild conditions, in particular for ligands sensitive to MeLi. Similarly, $[MePd(SMe_2)(\mu\text{-}I)]_2$ is a suitable precursor for the synthesis of neutral and cationic $MePd^{II}$ complexes, including [MePd(2,2′-bipyridyl)(γ-picoline)]BF_4, which has been characterized by X-ray crystallography.

Dialkylpalladium(II) complexes of nitrogen donor ligands are usually synthesized from alkyllithium reagents [1–6], either by reaction of the reagent with the dihalopalladium(II) complex [1–3], or by addition of ligand to a solution obtained on reaction of *trans*-$PdCl_2(SMe_2)_2$ with MeLi [4–6], although $\overline{CH_2CH_2CH_2\text{-}CH_2}Pd(bipy)$ has been obtained by reaction of 2,2′-bipyridyl with the tetramethylethylenediamine (tmen) complex [2] and $Et_2Pd(bipy)$ by reaction of $Et_2Al(OEt)$ with $Pd(acac)_2$ in the presence of bipy [7]. These routes require the ligand to be unreactive toward alkyllithium or alkylaluminium reagents [1–7], prior synthesis and characterization of dihalo complexes [1–3], or the use of donor ligands of sufficient basicity to displace bidentate tmen [2].

Pyridazine was chosen as a ligand in view of its low basicity, and we have found that $[Me_2Pd(pyd)]_n$ is a suitable precursor for direct synthesis of Me_2Pd^{II} and Me_3Pd^{IV} complexes containing ligands sensitive to MeLi. We have also demonstrated the convenient application of $[MePd(SMe_2)(\mu\text{-}I)]_2$ for the synthesis of

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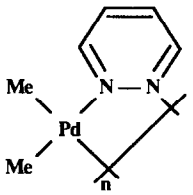

$[Me_2Pd(pyd)]_n$

$MePd^{II}$ complexes, including the γ-picoline complex $[MePd(bipy)(\gamma\text{-pic})]^+$ which has been characterized by X-ray crystallography.

The pyridazine complex was obtained by addition of 2.05 mole equivalents of halide-free methyllithium to *trans*-$PdCl_2(SMe_2)_2$ in diethyl ether (e.g. 1.5 g in ca. 130 ml) at ca. −60 °C under nitrogen, followed by addition of an ether solution of pyridazine at ca. −40 °C, hydrolysis at ca. −15 °C, and rapid filtration. The yellow-orange solid (70–80% yield) was washed with water and several portions of anhydrous ether, dried immediately under high vacuum at ambient temperature, and stored at ca. −20 °C. The complex exhibits a simple ^1H NMR spectrum in $(CD_3)_2CO$, consistent with the formulation $[Me_2Pd(pyd)]_n$ (Table 1), but decomposition takes place in solution during 10–15 minutes. Low stability prevented the determination of the value of *n* by osmometry in organic solvents.

The pyridazine complex reacts immediately and cleanly with PPh_3 in acetone at ambient temperature to give *cis*-$Me_2Pd(PPh_3)_2$ (55% yield on isolation, purification not necessary), illustrating its application in synthesis of phosphine complexes, and with bidentate nitrogen donor ligands containing ketone and alkene groups sensitive to MeLi to give $Me_2Pd(L)$ {L = (py)(mim)C=O, $(mim)_2C$=O, and (py)(mim)C=CH_2, where py = pyridin-2-yl and mim = *N*-methylimidazol-2-yl} (Table 1). The ligand (py)(mim)C=CH_2 is shown in Fig. 1.

Reports of hydrocarbylpalladium(IV) complexes are limited to a single neutral complex, *fac*-$Me_3Pd(bipy)I$, and four ionic complexes, [*fac*-$Me_3Pd(L')$]I (L′ = $(pz)_3CH$, $(pz)_2(py)CH$, $(pz)_2(mim)CH$, and $(py)_3CH$, where pz = pyrazol-1-yl), obtained on oxidative addition of iodomethane to the appropriate Me_2Pd^{II} complexes [5,6]. The complexes, and the new complex $Me_3Pd(phen)I$, may be isolated in ca. 45–67% yield directly from $[Me_2Pd(pyd)]_n$ on reaction with bipy, phen · H_2O, or L′ followed by MeI in acetone at 0 °C, so avoiding the need for prior synthesis and characterization of Me_2Pd^{II} complexes of the ligands; solutions of complexes *fac*-$Me_3Pd(L)I$ where L contain ketone or alkene groups were obtained similarly, or from $Me_2Pd(L)$ (e.g. Fig. 1), but isolation could not be effected before reductive elimination of ethane to form MePd(L)I had occurred.

Monoalkylpalladium(II) complexes of nitrogen donor ligands have been obtained by reaction of $(Me_3CCH_2)_2Pd(bipy)$ with benzyl bromide to give $Me_3CCH_2Pd(bipy)Br$ [3], reaction of MeMgI and the ligand with *trans*-$PdCl_2(SMe_2)_2$ at low temperature [4], reaction of $[MePd(SMe_2)I]_2$ [8] with the ligand for the synthesis of MePd(bipy)I and MePd(L′)I [5,6], and reaction of $[MePd(SMe_2)Cl]_2$ [8] with 2,9-dimethyl-1,10-phenanthroline for the synthesis of $MePd(Me_2phen)Cl$ [9]. We report here the utility of $[MePd(SMe_2)I]_2$ (obtained in 91% yield from *trans*-$PdCl_2(SMe_2)_2$ [8]) for the synthesis, at ambient temperature, of other classes of $MePd^{II}$ complexes, including a series of crystalline cationic complexes (Table 1).

Table 1

Yield and characterization data for complexes isolated [a]

Complex	Colour	Yield	^{1}H NMR	
			δ(MePd)	Solvent
Dimethylpalladium(II) complexes				
$[Me_2Pd(pyd)]_n$	yellow-orange	75	0.06	$(CD_3)_2CO$
cis-$Me_2Pd(PPh_3)_2$ [b]	white	55	0.20	$CDCl_3$
$Me_2Pd(bipy)$ [c]	yellow-orange	82	0.24	$(CD_3)_2CO$
$Me_2Pd\{(py)(mim)C{=}O\}$	yellow-orange	46	0.08, −0.06	$(CD_3)_2CO$
$Me_2Pd\{(mim)_2C{=}O\}$	orange	78	0.10	$(CD_3)_2CO$
$Me_2Pd\{(py)(mim)C{=}CH_2\}$	yellow	52	0.08, −0.10	$(CD_3)_2CO$
Methylpalladium(II) complexes				
trans-$MePd(PPh_3)_2Cl$ [d]	white	75	−0.03	$CDCl_3$
$MePd(bipy)Cl$ [e]	pale yellow	73	1.04	$CDCl_3$
$MePd\{(pz)_2CMe_2\}Cl$	pale yellow	57	1.04	$CDCl_3$
trans-$MePd(PPh_3)_2Br$ [d]	yellow	79	0.08	$CDCl_3$
$MePd(bipy)Br$	yellow-orange	75	1.04	$CDCl_3$
$MePd\{(pz)_2CMe_2\}Br$	yellow	66	1.03	$CDCl_3$
trans-$MePd(PPh_3)_2I$ [b]	white	82	0.23	$CDCl_3$
$MePd(bipy)I$ [f]	yellow	79	0.97	$CDCl_3$
$MePd\{(pz)_2CMe_2\}I$	yellow	73	0.98	$CDCl_3$
$MePd\{(py)(mim)C{=}O\}I$ [f]	yellow-orange	68	0.82	$(CD_3)_2CO$
$MePd\{(mim)_2C{=}O\}I$	yellow	88	0.77	$(CD_3)_2SO$
$MePd\{(py)(mim)C{=}CH_2\}I$ [g]	pale yellow	66	0.77	$(CD_3)_2CO$
[MePd(terpy)]I	orange	87	1.09	CD_3OD/ $(CD_3)_2SO$
$[MePd(bipy)(\gamma\text{-pic})]BF_4$	white	65	0.90	$(CD_3)_2CO$
$[MePd(bipy)(NCMe)]BF_4$	white	76	1.18	$(CD_3)_2CO$
$[MePd(bipy)(SMe_2)]BF_4$	white	63	1.00	$(CD_3)_2CO$
Trimethylpalladium(IV) complexes				
fac-$Me_3Pd(phen)I$	white	52	1.96, 1.20	$(CD_3)_2CO$
fac-$Me_3Pd(bipy)I$ and $[fac\text{-}Me_3Pd(L')]I$ [h]				

[a] All isolated new complexes have satisfactory ^{1}H NMR spectra, and microanalysis (C,H,N) except for $[Me_2Pd(pyd)]_n$ which is insufficiently stable at ambient temperature for postage for microanalysis. Previously reported complexes have ^{1}H NMR spectra in agreement with those reported [5,6,10,11]. [b] Previously reported [10]. [c] Previously reported [1,5]. [d] Previously reported [11]. [e] Previously reported, but synthetic method not given [12]. [f] ~ 90% Isomer with Me *trans* to mim, the other isomer has δ(MePd) 0.64. [g] ~ 93% Isomer with Me *trans* to mim, the other isomer has δ(MePd) 0.53. [h] All white, yield 45–67%, characterization data as reported earlier for preparation by a different route, bipy [5], and L′ = $(pz)_3CH$, $(pz)_2(py)CH$, $(pz)_2(mim)CH$, $(py)_3CH$ [6]. [i] Previously reported [5].

Neutral phosphine complexes are readily obtained, exemplified by isolation of *trans*-$MePd(PPh_3)_2I$ in 82% yield from acetone, and complexes of bidentate nitrogen donor ligands sensitive to MeLi are similarly obtained, e.g. $MePd\{(py)(mim)C{=}O\}I$. The complex $[MePd(SMe_2)I]_2$ is also a suitable precursor for the synthesis of bromo and chloro complexes. Thus, treatment of an acetonitrile solution with 2.4 mole equivalents of $AgNO_3$, followed by filtration to remove AgI, addition of 4.0 mole equivalents of KBr in a small volume of acetone/water with subsequent removal of the remaining Ag^+ as AgBr, and addition of L″ [bipy, $(pz)_2CMe_2$] or PPh_3 gave $MePd(L'')Br$ or *trans*-$MePd(PPh_3)_2Br$. A similar proce-

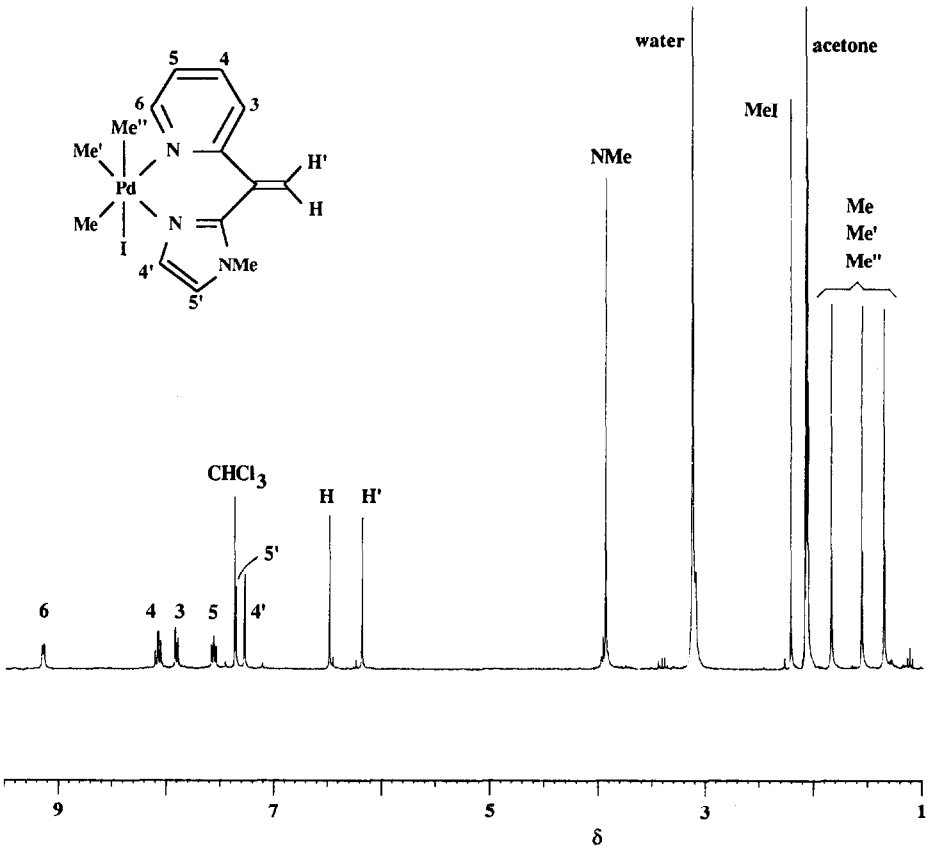

Fig. 1. The ^{1}H NMR spectrum of *fac*-$Me_3Pd\{(py)(mim)C{=}CH_2\}I$, obtained on addition of MeI to $Me_2Pd(py)(mim)C{=}CH_2\}$ in $(CD_3)_2CO$ at 0 °C. Integration is appropriate for the assignments given, and H and H′ were assigned using long range enhanced correlation spectroscopy. Similar spectra, but with addition of free pyridazine resonances, are obtained on addition of $(py)(mim)C{=}CH_2$ to $[Me_2Pd(pyd)]_n$ followed by MeI.

dure, but with the addition of ligand preceded by addition of water and additional KCl with stirring for 15 min, gave the chloro analogues.

The ionic complexes, [MePd(terpy)]I and $[MePd(bipy)(\gamma\text{-pic})]BF_4$, are obtained on addition of 2,2′:6′,2″-terpyridyl to $[MePd(SMe_2)I]_2$ in acetone, or addition of bipy followed by $AgBF_4/\gamma$-picoline with subsequent filtration to remove AgI followed by crystallization of $[MePd(bipy)(\gamma\text{-pic})]BF_4$. An attempted preparation of $[MePd(bipy)(NCMe)]BF_4$, by this procedure gave $[MePd(bipy)(SMe_2)]BF_4$, but the acetonitrile complex may be readily isolated on treatment of MePd(bipy)I with $AgBF_4$/NCMe and filtration to remove AgI.

Crystals of the γ-picoline complex suitable for a structural study were obtained by dissolution of the complex in acetone, assisted by the minimum quantity of dichloromethane, followed by exposure to diethyl ether vapour in a sealed chamber at ambient temperature. Crystals of $[MePd(bipy)(\gamma\text{-pic})]BF_4$, $C_{17}H_{18}BF_4N_3Pd$, M = 457.6, are monoclinic, space group $P2_1/n$ with a 8.243(2), b 12.632(4), c 17.550(5) Å, β 95.75(2)°, U 1818.2(8) Å^3, D_c 1.67 g cm^{-3}, and $Z = 4$. 3216 Independent data

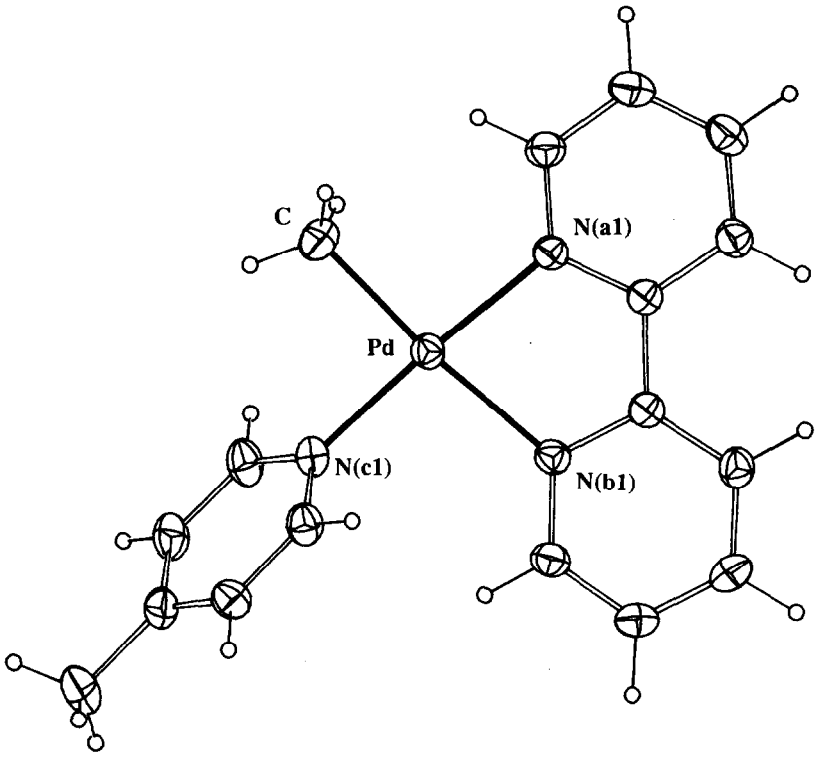

Fig. 2. The cation $[MePd(bipy)(\gamma\text{-pic})]^+$ projected normal to the '$PdCN_3$' coordination plane; 20% thermal ellipsoids are shown for the non-hydrogen atoms, and hydrogen atoms (constrained at estimated idealized positions) have been given an arbitrary radius of 0.1 Å. Selected bond distances and angles: Pd–C 2.036(6), Pd–N(a1,b1,c1) 2.049(4), 2.131(4), 2.033(4) Å, C–Pd–N(a1,b1,c1) 95.4(2), 174.3(2), 88.1(2)°, N(a1)–Pd–N(b1,c1) 79.1(2), 176.4(2)°, N(b1)–Pd–N(c1) 97.4(2)°.

were measured with a Syntex $P2_1$ four-circle diffractometer in conventional $2\theta/\theta$ scan mode ($2\theta_{max}$ 50°) with Mo-K_α (0.7106_9) Å) radiation. Full matrix least squares refinement converged at R and R' of 0.039 and 0.041 for the 2368 absorption corrected reflections having $I > 3\sigma(I)$ *.

The $[MePd(bipy)(\gamma\text{-pic})]^+$ cation, shown in Fig. 2, has square planar geometry for palladium, with bipy forming the smallest bond angle (N(a1)–Pd–N(b1) 79.1(2)°) and the carbon atom exhibiting the largest deviation from the 'CN_3' weighted mean plane (0.037 Å); the γ-picoline group forms a dihedral angle of 62.1° with the 'CN_3' mean plane.

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* The atomic coordinates, bond lengths and angles, and thermal parameters are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by a full literature citation for this communication.

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