Inorganica Chimica Acta, 100 (1985) L13–L14

Synthesis of Pyridine Ligands via Transient Organomercurials

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Received January 4, 1985

In recent years we have synthesized several 2-pyridylmethane ligands, *e.g.* py_2PhCH [1], in studying the coordination chemistry of organometallic cations [1–3]. As the synthesis of these ligands involves organolithium intermediates, *e.g.* $pyPhCH^-Li^+$, where the anions are related to ligands such as Ph_3C^- [4] and $py(Me_3Si)_2CH^-$ [5], we have commenced a study of the interaction of anions of 2-pyridylmethanes with metal ions.

Preliminary studies involving interaction of organolithium derivatives with mercury(II) iodide have led to isolation of dimers, as shown below and in Table I.

$$pyRR'CH \xrightarrow{(i), (ii), (iii)} (pyRR'C)_2$$

(i) 1 Bu^nLi/hexane/THF, (ii) ½ HgI_2/THF, (iii) H_2O

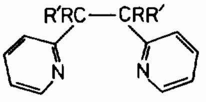
As the dimers are ligands of possible wide applicability in coordination chemistry, *e.g.* $(pyPhCH)_2$ as a pyridine analogue of stilbenediamine, $((NH_2)PhCH)_2$ [6], some preliminary results are reported here.

In a typical synthesis, n-butyllithium in hexane was added to 2-benzylpyridine in tetrahydrofuran under nitrogen, to give a blood-red solution of $pyPhCH^-Li^+$. Addition of mercury(II) iodide in THF resulted in complete loss of colour and precipitation of mercury. On hydrolysis, removal of solvents under vacuum, and extraction of the residue with boiling ethanol followed by filtration, colourless crystals of $(pyPhCH)_2$ formed on volume reduction. Recrystallization from ethanol resulted in an overall yield of 80%.

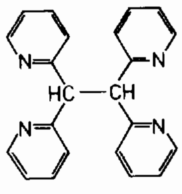
TABLE I. Dimerization of 2-Pyridylmethanes.

Reagent	Dimer[a]	Mol. Wt[b]	M. Pt. (°C)	Yield[c] (%)
$pyMe_2CH$	$(pyMe_2C)_2$	245(240)	116–117[d]	16
$pyPhCH_2$	$(pyPhCH)_2$	350(336)	240–242[e]	80
pyMePhCH	$(pyMePhC)_2$	358(364)	131–134	42
py_2CH_2	$(py_2CH)_2$ [f]	327(338)	*ca.* 300	85

[a] Dimers have appropriate microanalyses (C, H, N) and ^1H NMR spectra in $CDCl_3$, *e.g.* (i) presence of one methine singlet for $(pyPhCH)_2$ and $(py_2CH)_2$, and absence of methine protons for $(pyMe_2C)_2$ and $(pyMePhC)_2$, (ii) a single pyridine H(6) resonance for each dimer. [b] Osmometrically in chloroform at 37 °C, calculated values in parentheses. Mass spectra exhibit appropriate parent ions. [c] To date, reaction conditions have not been extensively developed to maximize yields. [d] Lit. value 121 °C [7]. [e] Lit. values 244–245 [8], 243–244 [9], 240–241 °C [10]. [f] Reflux required.



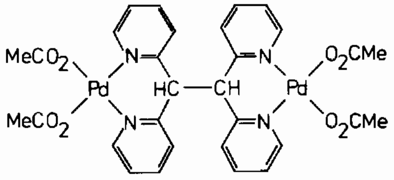
R = R' = Me
R = H, R' = Ph
R = Me, R' = Ph



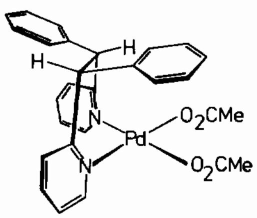
$(py_2CH)_2$

The dimers are apparently formed from transient diorganomercurials which decompose to mercury and radicals, *e.g.* as found on pyrolysis of dibenzylmercury, forming mercury and dibenzyl [11]. Consistent with this interpretation, $(pyPhCH)_2$ has also been prepared (in 30% yield) from radicals $pyPhCH^•$ formed on treatment of $pyPhCH_2$ with t-butoxy radicals [9].

In preliminary studies, complexes of $(py_2CH)_2$ and $(pyPhCH)_2$ with palladium(II) acetate have been isolated from benzene solutions under nitrogen*. The dimer $(py_2CH)_2$ forms a complex of stoichiometry $(Pd(O_2CMe)_2)_2(py_2CH)_2$ in which the ligand binds as a bidentate to two $Pd(O_2CMe)_2$ moieties, and $(pyPhCH)_2$ forms a complex of stoichiometry $Pd(O_2CMe)_2(pyPhCH)_2$.



$(Pd(O_2CMe)_2)_2(py_2CH)_2$



$Pd(O_2CMe)_2(pyPhCH)_2$

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*The complexes have appropriate microanalyses (C, H, N), ^1H NMR spectra in $CDCl_3$, and infrared spectra, *e.g.* $\nu(CO_2)$ 1640, 1314 and 1634, 1312 cm^{-1} for $(py_2CH)_2$ and $(pyPhCH)_2$ complexes indicative of unidentate acetate coordination [12].

0020-1693/85/$3.30

Although the dimer $(pyPhCH)_2$ is assumed to be formed in both racemic and meso forms, ^{1}H NMR spectra of the complex isolated (low yield) are consistent with the presence of the meso form only. Thus, two acetate and two methine environments are present, with decoupling of methine protons ($J = 13$ Hz) indicating that the methine resonances arise from protons within the same complex. Simple molecular models suggest that the meso form has lower intramolecular steric interactions than a complex of the racemic form of the ligand.

Acknowledgements

This work was supported by the Australian Research Grants Scheme and the University of Tasmania.

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